REFINER
AND NATURAL GASOLINE MANUFACTURER
A Gulf Publishing Company Publication

VOLUME 11, No. 8 AUGUST, 1932

Speed The Five-Day Week

THE petroleum industry should be first to adopt the five-day week. Some of its larger units have instituted this shorter working period but it lacks universal adoption. Evidently there are men who still expect "things to get better." But the shorter set of working hours offers a method of forcing conditions to get better.

The five-day week amounts almost to a national policy. It has the approval of President Hoover, who has called business leaders into conference to determine how it can be accomplished. If all the instances of its adoption could be enumerated no doubt the showing would be impressive. That the plan has growing popularity is evident. All it needs now is a growing adoption.

Unless the workers come out of this depression with shorter working hours as their privilege the sufferings of the past three years will have gained but little. It is the worker who deserves first consideration in the shorter week. He has had too little of work but that is not reason that the future should give him too much work.

Recent reports place the number of unemployed in the United States at more than ten millions. There is evidence of a change in the course of business now but it will take many months to furnish employment for ten million men and women. By reducing the hours per man this task of finding places for these millions will be shortened.

When this figure is studied the wonder arises that there has been so little unrest in the United States. The workers of this country deserve praise for their attitude. Their patience has been tried to the hurting point and it will be tried for many more months. Those charged with providing labor deserve praise for the efforts made to keep men working in spite of a diminishing demand for goods.

Efforts of the petroleum industry to give more men employment through shorter working hours is almost as old as the depression. The Sunday shutdown was one of the first such moves and certain concerns applied it in the oil fields, where its adoption was difficult.

One of the difficulties was that other concerns did not adopt such hours. It is difficult to refuse to do business when other concerns and other industries insist on keeping open as in those days prior to October, 1929.

Now, however, there is a movement which can make Saturday a day of idleness. Some wheels must turn regardless of the day, but American industry can reduce its Saturday activity to match that of Sunday if it will take hold of the five-day week as it should.

The petroleum industry has a second interest in this five-day week. A week of that much labor means a week with two days of leisure. More than any other industry, petroleum thrives on chances for pleasure. Give the American public two days of leisure each week and some consumption records on gasoline will be written to make small figures of anything previously known.

There is a falling off in automobile use now but that is temporary. The American people have been put on wheels and they will not go back to the ox cart or the horse and buggy. These may serve for a spell but the ambition of each family is to own an automobile. That goal had about been reached when the business world turned topsy turvy three years back. So long as that desire remains there is assurance that the goal will be reached.

Give each American family its automobile and two days of leisure each week and the use of gasoline will soar to figures to gladden the eyes of those charged with studying consumption curves.

So the petroleum industry has its dual interest in the five-day week. From the humanitarian standpoint it should match what other industries are willing to do. From a selfish viewpoint it should take the lead, for it stands to profit by providing men and women with the leisure that will allow the use of its merchandise.

SYNTHETIC AMYL Alcohols and Amyl Acetates *Start from the* Chlorination of Pentane

H. A. BOHALL
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AT Belle, West Virginia, Sharples Solvent Corporation operates the only plant of its kind in the world where amyl alcohols and amyl acetates are synthetically produced. Production of these products in this plant was begun in the fall of 1926, and, although many changes have occurred during the six years of operation, still the basic principle of operation is the same.

Briefly the operation may be described as consisting of three steps:

(1) Chlorination of the pentane to form amyl chloride

$$\underset{\text{Pentane}}{C_5H_{12}} + \underset{\text{Chlorine}}{Cl_2} = \underset{\text{Amyl Chloride}}{C_5H_{11}Cl} + \underset{\text{Hydrochloric Acid}}{HCl}$$

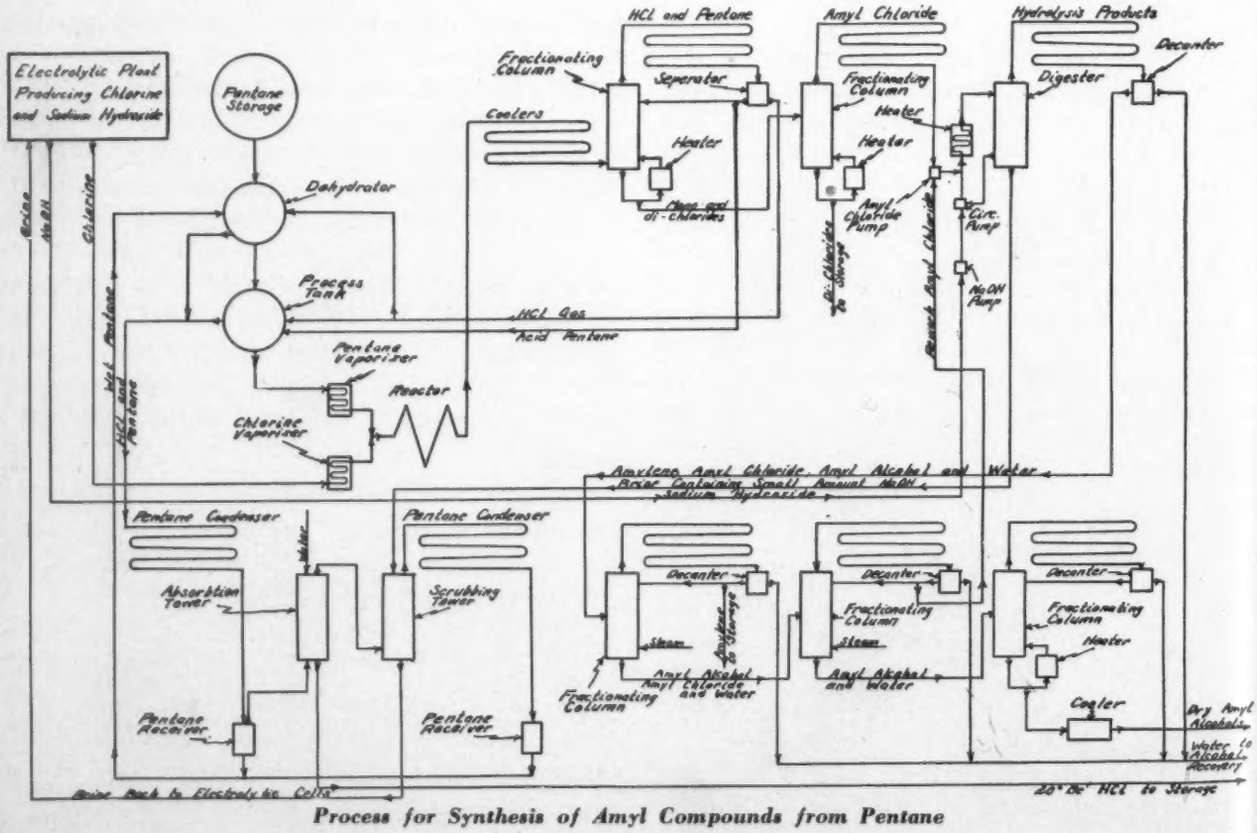
(2) Hydrolysis of the amyl chloride to produce amyl alcohol as indicated by the following reaction in which an aqueous solution of caustic soda is employed in the presence of a catalyst of oleic acid.

$$\underset{\text{Amyl Chloride}}{C_5H_{11}Cl} + \underset{\text{Sodium Hydroxide}}{NaOH} = \underset{\text{Amyl Alcohol}}{C_5H_{11}OH} + \underset{\text{Sodium Chloride}}{NaCl}$$

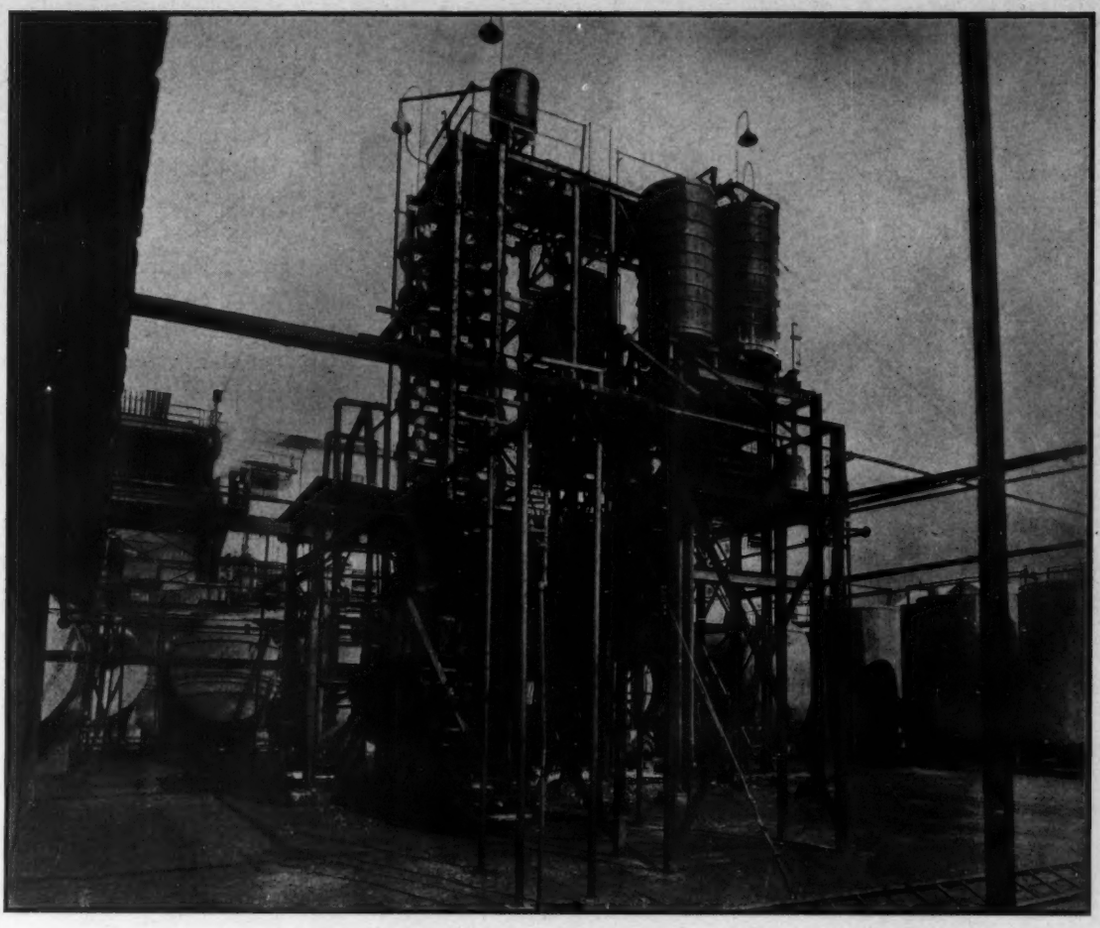
(3) Acetylation of Amyl Alcohol to produce Amyl Acetate.

$$\underset{\text{Amyl-Alcohol}}{C_5H_{11}OH} + \underset{\text{Acetic Acid}}{CH_3COOH} = \underset{\text{Amyl Acetate}}{CH_3COOC_5H_{11}} + \underset{\text{Water}}{H_2O}$$

But, when we consider that the pentane used con-



Process for Synthesis of Amyl Compounds from Pentane



Equipment for Absorption of Muriatic Acid from Pentane

sists of two of the possible three isomers and the resutling products are composed of six of the possible seven isomeric chlorides, six isomeric alcohols corresponding to these chlorides and five acetates, some of the complications involved in the complete process appear. Add to this, the formation of by-products occurring from side reactions and polymerization and a more complete picture of the problem is obtained and it is realized that while these three steps serve to outline the procedure still by no means do they tell the complete story.

The Sharples plant was designed and constructed to produce amyl alcohols and amyl acetates to meet the ever increasing demand for high boiling lacquer solvents occasioned by the rapid advancement in the development of lacquers for use in the automobile industry. Fusel oil and fusel oil acetates were employed for this purpose. The fusel oil is obtained as a by-product of ethyl alcohol manufacture and can not be obtained in sufficient quantities to meet the market's rapidly expanding demands and so the development of the synthetic products was sought.

Previous laboratory experiments in the chlorination of hydrocarbons had indicated the practicability of chlorinating pentane at temperatures above 200°C., 392°F.) in the absence of light and without the use of a catalyst. Hence, the plant was designed for the commercial application of this reaction. The successful plant operation of the past six years has more than justified the laboratory experiment.

CHLORINATION

In the chlorination plant there are only two raw materials required—chlorine and pentane. The former is liquid chlorine obtained by pipe line from a chlorine plant located on the adjacent factory site. This chlorine is carefully tested for water and moisture content maintained below 1000 parts per million as the presence of moisture causes corrosion of proccess equipment. The pentane, although at one time necessitating special fractionating equipment for its preparation, is now available from several of the larger gasoline refineries in sufficiently close cuts to be chlorinated without further fractionation. This pentane is the fraction (boiling 27°—40°C. or 80.6—104°F.) from natural gas gasoline and consists principally of normal pentane and isopentane in approximately equal proportions with a small amount of butane and hexane present as impurities. This pentane is received in tank cars and unloaded by gravity to the storage tanks from which it is pumped as desired to a dehydrator and after drying passed to the process tanks. From the process tanks the

Equipment for Hydrolysis of Amyl Chlorides, showing Digesters and Circulating Pumps

dry pentane is pumped continuously to the chlorination unit.

Both the chlorine and pentane are passed through steam heated vaporizers to convert them to the vapor state before mixing. Mixing is effected by introducing the vaporized chlorine into the sides of a Venturi nozzle through which the pentane passes on its way from the vaporizer. The expansion resulting from passing through the nozzle affords the high velocity which is necessary for intimate mixing. The pentane at the throat has a velocity of one mile per minute and 92,000 gallons pass through the throat daily. Yet only three gallons are present at any one moment and not over eight ounces of uncombined chlorine is in contact with pentane at any given moment, and still 18 to 24 tons of chlorine are reacted daily. All this is due to the speed of the reaction which is completed in 2½ seconds.

From 15 to 20 parts pentane to each part chlorine is circulated. This insures thorough mixing and decreases hazard of burning in the throat. Temperatures at mixing are necessarily kept low to inhibit reaction before mixing is complete as this tends to increase the formation of undesirable polychlorides.

Immediately after mixing, the gases are passed to a gas-heated pipe still consisting of a series of manifolded harps. Heating here to 260°C (500°F.) accelerates the reaction, but in order to keep the formation of undesirable polychlorides at a minimum it is important that the time of heating be very short. Hence, the gases are passed immediately to a bank of pipes cooled by water spray and chilled sufficiently to stop further reaction before passing to the fractionating towers.

During this process of chlorination, two by-products, both undesirable, may be formed:

(1)—Amylene from the breaking down of amyl chlorides

$$C_5H_{11}Cl = C_5H_{10} + HCl$$

(2)—Polychlorides from the further chlorination of amyl chloride.

Employing lower temperatures and higher pressures tends to keep the amylene formation at a minimum. However, this can never be entirely eliminated. Any amylene formed will remain with the uncombined pentane on recycling and will be instantly converted to dichloride on the next cycle according to the following reaction:

$$C_5H_{10} + Cl_2 = C_5H_{10}CL_2$$

Efficient fractionation of the amyl chloride from the pentane keeps the amount of amyl chlorides recycled to a minimum and hence precludes the formation of polychlorides by the direct chlorination of amyl chloride.

The exit gases from the pipe still, after cooling, are passed to the first of four continuous fractionating columns of conventional bubble-cap design. This first column is so operated by maintaining a high reflux ratio as to permit nothing but excess pentane and the hydrochloric acid formed in the reaction to pass off overhead. This mixture is returned to the process tank at the start of the system from which the pentane is recycled to the vaporizer and part of the hydrochloric acid is withdrawn to the dehydrator for drying pentane, the balance of the hydrochloric acid going to the recovery plant.

The bottom product from the first fractionating tower is pumped to a second tower. This product is a mixture of amyl chlorides and unreacted pentane. The overhead product from this column is rich in pentane and is returned to the feed of the first column while the bottom product which is of high chloride content and contains little pentane is passed to the third column. In this column the dichlorides

and higher products are removed from the base to a separate still not run continuously while the overhead product of amyl chloride and small amount of pentane is removed to a fourth column from the base of which relatively pure amyl chloride is drawn to storage, the pentane-amyl chloride overhead product being returned to feed of first column.

The dichlorides and more highly chlorinated products drawn off from the base of the third column above are caustic distilled in the discontinuous still by batch process as a charge is accumulated and the dichlorides sent to storage while the tarry residue remaining is wasted.

HYDROCHLORIC ACID RECOVERY

For every atom of chlorine that combines with an atom of pentane one molecule of hydrochloric acid is formed. As mentioned above this hydrochloric acid passes off in the product taken overhead from the first column in the chlorination plant together with the unreacted pentane and is returned to the process tank.

A portion of this hydrochloric acid is drawn off to the dehydrator and bubbled up through the pentane where it combines with any water that is present in the pentane to form aqueous hydrochloric acid which settles to the bottom of the dehydrator from which it is drawn to the sewer periodically. Thus a thoroughly dry pentane is drawn off at a slightly higher level to the process tank. In this manner, the pentane is effectually dried by using only a small portion of one of the reaction products and introducing no extraneous drying agent.

The dry hydrochloric acid not passed to the dehydrator and that not taken up by the water in the dehydrator is passed through a condenser where the greater part of the pentane is condensed and removed, and thence through a double counter-current system of silica tourills where it is absorbed in water. This hydrochloric acid absorption unit differs from conventional designs only in that it is operated at sufficiently high temperature to keep any pentane volatilized. The flow of water is adjusted so as to deliver hydrochloric acid of a strength corresponding to 20° Be. to a twin set of rubber lined blow-cases which are alternately blown to tank cars or storage. The grade of hydrochloric acid produced is the very best, as it is free from sulphates and all impurities except traces of iron.

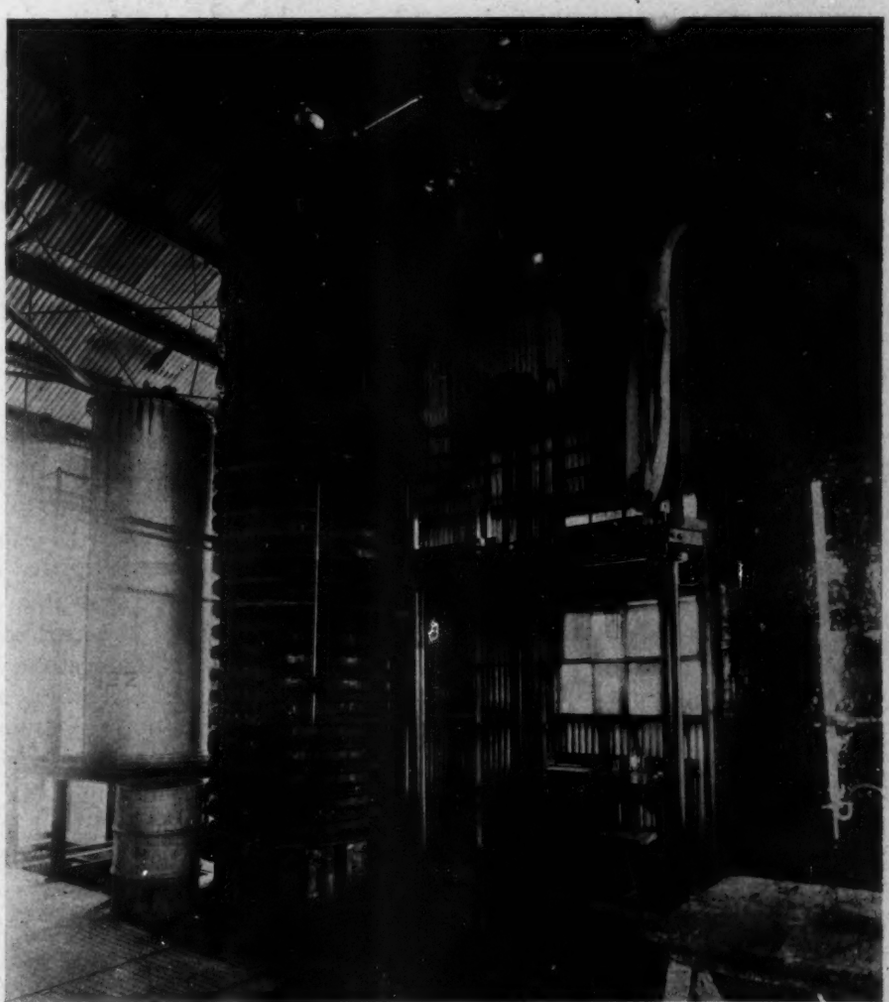
The unabsorbed gas which is chiefly pentane is next scrubbed with slightly alkaline brine withdrawn from the digesters in the subsequent hydrolysis operation. The neutral gas is then compressed and the liquid pentane returned to the dehydrating tank for recycling. Neutral brine from the scrubbers is returned to the chlorine plant for use in the electrolytic cells for generating more chlorine.

HYDROLYSIS

The amyl chlorides drawn off from the base of the fourth column in the chlorination plant is a mixture of six isomers. Ninety-five per cent of these mixed chlorides distill on Engler distillation between 85° and 107°C, (185 and 224.6°F.) and the only impurities present are the amylenes.

These mixed amyl chlorides are converted to the amyl alcohols by hydrolysis with aqueous caustic soda in the presence of oleic acid which serves as a catalyst.

This process is continuous and is carried out in two digesters connected in series with agitation sup-



Equipment—Acetylation of Amyl Alcohols
Left to Right—Feed Tanks for Alcohols and Acetic Acid, Distillation Column for Continuous Acetylation, Column for Rectification of Crude Amyl Acetate.

plied by circulating pumps. Heat is supplied to the reaction mass as it passes through steam heaters placed in the circulating line.

One of these digesters is maintained full and to this digester the amyl chlorides and a 12-15 per cent caustic solution are pumped continuously. This caustic is purchased from the neighboring electrolytic plant as approximately 30 per cent and diluted as required to meet the needs of the digesters.

The other digester is carried only partly full and from the vapor space of this digester the products of hydrolysis together with any unreacted chlorides, water and amylenes are continuously distilled.

Circulation is from the top of one to the bottom of the other so that the caustic and chlorides have maximum opportunity for intimate contact. This contact is further enhanced by the oleic acid added as a catalyst.

The choice of a catalyst was one of the details that required much experimentation before being finally developed to the present state of satisfaction. To begin with, the amyl chloride is a mixture of six different isomers. These chlorides are very different in their behavior toward hydrolysis. The tertiary hydrolyses with water with comparative ease, the secondaries react less readily and the primaries not at all. Alkaline solutions do not change the respective behavior of the three classes toward hydrolysis but in the case of those two which do hydrolyse the presence of an alkali is desirable for removing the hydrochloric acid formed. Increasing the temperature and ensuring intimate collodial contact does not effect hydrolysis of the primary amyl chlorides.

Sodium oleate which is readily formed by the reaction of the caustic on the oleic acid was found to be a satisfactory medium as it was beneficial in the case of all three classes of chlorides. With the organic compounds present, sodium oleate forms a gel which holds water in suspension and thus serves to disperse the water throughout the digester mass and so bring it into intimate contact with the tertiary and secondary chlorides thus promoting hydrolysis of these two classes. Moreover, sodium oleate is itself in intimate contact with the secondary and primary chlorides thus affording them every opportunity to convert to amyl oleate and amyl oleate hydrolyzes readily to amyl alcohols in the presence of caustic.

Careful control by the laboratory keeps the operators informed of the composition of the digester mass at all times and the feed of caustic and amyl chlorides, which is from weight tanks, can be varied according to laboratory reports so as to keep the composition of the digester mass at all times within well appointed limits.

Some oleic acid is lost in withdrawals of brine and taking samples, etc. so that it is necessary occassionally to add fresh acid to replace the deficiency. All oleic acid collecting in the brine tanks is reworked by boiling with sulphuric acid, washed acid free and recovered for reuse in the digesters so that the consumption of oleic acid is very small.

The circulation by means of outside pumps and dispersion effected by the oleic acid does away with the trouble always encountered in agitator mixing where high pressures and temperatures are employed in the processing of volatile materials. Loses are thus reduced as well as the depreciation of equipment.

The heaters themselves are made with 180° Tube-Turns and are of welded construction throughout. This reduces corrosion and plugging of heater pipes and reduces the chances of leaks accordingly.

The product continuously distilled from the second digester is a mixture of amylenes, amyl chlorides, amyl alcohols and water. Amylene is formed from the breaking down of amyl chloride. Hydrolysis is never 100 per cent complete, which accounts for the amyl chloride, and the water is introduced in the caustic solution.

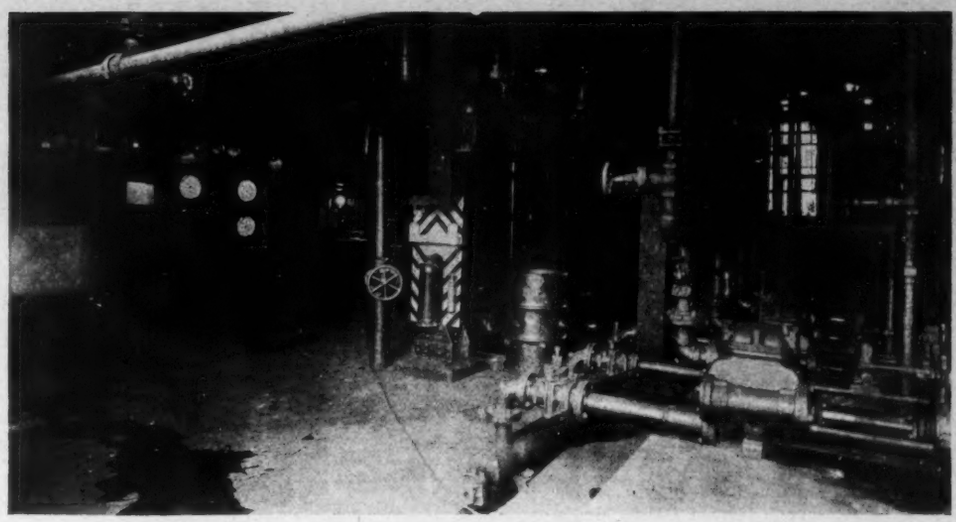
FRACTIONATION OF DIGESTER PRODUCTS

The next problem is the separation and fractionation of these products. This is effected in a series of three fractionating columns, each operated according to the material it is designed to handle. The first column removes the amylene as an overhead product.

The second column removes the amyl chloride. In the early days, when this operation was carried out as a batch process, it was found extremely difficult to effectively separate the amyl chloride and alcohols. In spite of repeated fractionation and painstaking endeavors, the dry amyl alcohol contained traces of amyl chloride. It was learned, however, that the wet distillation employed in the preliminary dehydration always carried the major portion of these chlorides. In this way it was discovered that there really was a three component constant boiling mixture of alcohol, amyl chloride and water. Advantage was taken of this and now this second column is heated continuously by live steam introduced through a sprager line, which not only furnishes the necessary heat but at the same time supplies the water required for the formation of this constant boiling mixture. The overhead product is passed through a decanter from which the undissolved water is continuously drawn and sent to a still employed for recovering all oils from water solutions from all processes, while the amyl chloride-alcohol mixture is returned to the digester for retreatment.

The bottom product from this second column is fed to a third column which delivers a dry alcohol at the base and passes a constant boiling alcohol-water mixture overhead to a decanter from which the oil layer is returned to the first column and the water sent to the recovery still. The dry alcohol

from the base is passed to crude alcohol storage tanks from which it is withdrawn in batches for rectification.



Equipment for Chlorination, Showing Battery of Circulating Pumps and Instrument Panel for Control.

RECTIFICATION OF ALCOHOLS

In the rectification of the crude alcohols we have the first batch process in the manufacture of the alcohols, everything having been continuous heretofore. Since there are produced six different alcohols, this part of the operation is done by batches and cuts made according to the demands of the market. The tertiary alcohol is first removed and ordinarily the balance distilled over without further fractionating. The mixture of the five remaining alcohols is marketed under the trade name of "Pentasol."

To meet the special requirements of some customers close-boiling cuts of normal butyl carbinol, secondary amyl alchol, isobutyl carbinol, methyl propyl carbinol or diethyl carbinol are either taken out directly or a cut rich in the alcohol desired accumulated and refractionated. A water-soluble cut with a boiling range of 128°—132°C. (262.4°—269.6°F) is also prepared in a separate unit by first extracting the water soluble portion and then dehydrating and fractionating.

The residue accumulating in the rectification still is accumulated until a batch is on hand. It is then stripped of all alcohol by straight distillation, after which it is steam distilled to recover the amyl ether, a small amount of which is formed in the process. Also from this residue there is recovered any oleic acid that has inadvertently been carried through from the digesters.

ACETYLATION

Since the tertiary amyl alcohol has a tendency to decompose on acetylation, this alcohol is removed from the product to be used for acetylation as described above. The secondary alcohols are present in too great a proportion to make their removal practical.

Equipment for the acetylation of the "Pentasol" is standard in design and consists simply of a copper kettle and fractionating column with auxiliary feed tanks for alcohol and acetic acid.

This process is continuous. The reaction is strictly reversible and to force it to proceed in the desired direction the water formed is removed. Sulphuric acid is employed as a catalyst. A low concentration of acetic acid in aqueous solution is maintained in the kettle and amyl alcohol and acetic acid fed in in approximately reaction proportions. Overhead a mixture of amyl acetate and unreacted alcohol and water is continually removed and a high reflux on column keeps the acetic acid washed back to the kettle.

The crude ester taken off runs about 65 to 70 per cent ester. It is slightly acid and hence is dropped to a neutralizing tank where it is treated with soda ash to neutralize all free acid before final rectification.

RECTIFICATION OF AMYL ACETATE

Here again a batch process is employed. The equipment is a steel kettle with a copper fractionating column. Fractionation is carried on slowly until the heads containing chiefly alcohol are removed, then take-off increased and the batch rapidly distilled and dropped to receiving tanks. Here it is blended with other batches to meet shipping specifications and pumped to storage or tank cars for shipment.

The heads taken off are returned to the acetylation unit for reacetylation to build the ester content up. Laboratory control enables the operator to run these heads in with the regular alcohol feed without upsetting the kettle balance.

The acetylated alcohols is a mixture of five isomeric amyl acetates and marketed under the trade name of "Pentacetate."

In connection with the main plant, the operation of which is devoted to the production of Pentasol and Pentacetate, there is maintained an experimental plant. Here there is a complete unit for experimental chlorination, several stills and columns for fractionation work of all kinds.

Several new products are being produced on a small scale in this section of the plant and research work is being conducted on several others which it is expected will result in the development of new uses and new fields for the now established products, the manufacture of which has been herein described.

Brunn-Koenigsfeld Type Pipe Still Erected At Fiume, Italy

DIRECTOR RICHARD NEUMAN
Brunn-Koenigsfeld
Translated from Petroleum Zeitschrift

RAFFINARIA di Olii Minerali Soc. Anon., has erected at Fiume, Italy, a pipe still for crude oil distillation, which contains many novelties and is the last word in applying the principles of distillation to commercial oil practice. This still has been erected in conjunction with its modernization program, and has replaced a battery of crude oil stills that have been in operation there for the past 40 years.

The design and erection of this new equipment was carried out by Brunn-Kralovo-Pol'er Machine and Car Works, A. G., of Brunn-Koenigsfeld, C. S. R.

In Figure 1 is shown the flow sheet of this pipe still. By means of crude oil pump L and through heat exchangers G. H. K., crude oil is pumped into the system and it enters the pipe still A preheated to an inlet temperature of 400°F. In the coils of the pipe still the oil is further heated both by radiation and conduction, and the heat input is sufficient to vaporize 93 per cent of the total crude entering the system. Upon leaving the pipe still, the crude and its vapors have reached a temperature of 790°F.

The stack gases leave the still comparatively cool due to the arrangement of allowing the incoming crude to flow countercurrent against the gases. Just before entering the furnace proper, the crude has been in contact with the hottest portion of the exit still gases.

The fuel oil used is that obtained from a Holmes-Manley cracking still nearby. The cracking plant was also erected by the same firm as mentioned above. When prices warrant, the soft grade of asphalt made in the pipe still is used as fuel, after being heated to thoroughly liquefy it.

The furnace of the pipe still is also so arranged as to contain a set of steam superheater coils, the latter receiving the entire waste refinery steam from pumps, etc., superheating it to a high degree, and making it available for steam rerun operations or for use in the steaming columns.

The material leaving the coils of the pipe still contain 93 per cent of the total crude as vapor and seven per cent asphaltic bottoms, and passing through the transfer line it enters the first of two modern bubble towers. Here the seven per cent asphaltic residue is withdrawn and the desired side streams are obtained as overhead cuts at the side of the tower. The asphalt is drawn off by a pump controlled by liquid level controls, while the ascending vapors follow up through a large number of adjustable bubble cap plates, where the narrow fractionation into cuts takes place. Usually a kerosene cut is refluxed over this tower in such quantities for making certain products, which are at the present time of operation: Gas oil; light paraffin distillate (contains pressable wax); and heavy paraffin oil distillate. The latter stock is used to further refine high viscosity motor and cylinder stocks.

The vapors not condensed in the first tower, and which consist of light and heavy gasoline fractions as well as kerosene are next passed through exchanger H and then enter the second fractionating tower. This tower separates light benzine, white spirit, and kerosene. This separation is accomplished by refluxing benzine distillate over the tower by means of pump N.

The light benzine leaves the tower partially as a vapor, but loses its heat and is further condensed in the crude oil exchanger G. The towers are equipped with stripping columns in which any of the above cuts may be passed and by the use of a small amount of steam injected into these strippers, a further removal of light ends can be obtained, and bottoms products from the strippers may be made to comply with special flash tests, viscosities, and so forth. The cuts from the stripping columns are liquid when they enter the final coolers by means of float controls.

It is especially these stripping columns that lend great flexibility to the whole fractionation arrangement, and which the Brunn-Koenigsfeld concern has shown to be adaptable not only for rapid changes in making new products from time to time, but also flexible to any change in the base or type of crude that might be available.

The towers are so arranged that any further number of bubble cap trays may be inserted between those present, or any number may be moved closer or further apart. This allows a great number of exceedingly pure cuts that may be obtained, and the proceedure in general is not common in American or other European plants, as far as the writer is aware. This success in obtaining narrow cuts is simplified by the use of auto-

matic valve control, using the float and liquid level control principle.

PREHEATER

Of especial interest is the preheater H which condenses the greater part of the kerosene necessary for efficient fractionation in the first tower from the vapors which leave No. 2 tower. The heat given up by the kerosene vapors in cooling is absorbed by cool incoming crude, and this of course makes for a great saving in thermal efficiency of the whole plant. Indirectly this allows a minimum of reflux benzine necessary for fractionating in tower No. 2. Great saving of cooling water for the condensers thus results, and this is due again to the small amount of benzine which is still in vapor form.

All of the pumps, such as feed, reflux and residue pumps are so arranged that they may be operated in a few minutes by steam instead of electrical current.

Throughout the plant great stress is laid upon the complete accuracy of all the temperature control devices, automatic controls, and steam regulators, and this has resulted in the employment of very few men that are actually needed to run the still. The usual control-board room seen in other refineries is housed in a small building, and here accurate control is provided for.

At present Grosny crude is run and the following finished products are obtained:

LIGHT BENZINE

Sp. Gravity	0.731
I. B. P.	122°F.
E. PT.	350°F.

WHITE SPIRIT

Sp. Gravity	0.790
I. B. P.	327°F.
E. PT.	390°F.
Flash, Abel	106°F.

KEROSENE

Sp. Gravity	0.820
I. B. P.	400°F.
E. PT.	548°F.
Flash, Abel	183°F.

GAS OIL

Sp. Gravity	0.849
I. B. P.	560°F.
E. PT.	680°F.
Visc. about	2.0 E at 20 Cent.
Flash open cup	295°F.
Pour point, Pohl	46°F.

LIGHT PARAFFIN OIL

Sp. Gravity	0.871
Visc. 50C.	1.8 Eng.
Flash open	300°F.
Pour, Pohl	83°F.

HEAVY PARAFFIN OIL

Sp. Gravity	0.920
Visc. 100 Cent.	2.8 Eng.
Flash, open cup	482°F.
Pour, Pohl	122°F.

ASPHALT

Sp. Gravity	over 1.00
M. P. Kramer-Sarnow	118-122°F.
Flash, open	648°F.

Although this plant has now been operated continuously for the past two months at the relatively high transfer-line temperature of 788°F., not a trace of coke or free carbon has been found in the tubes or on the plates in the towers. This is proof that the distillation is taking place without the presence of cracking reactions.

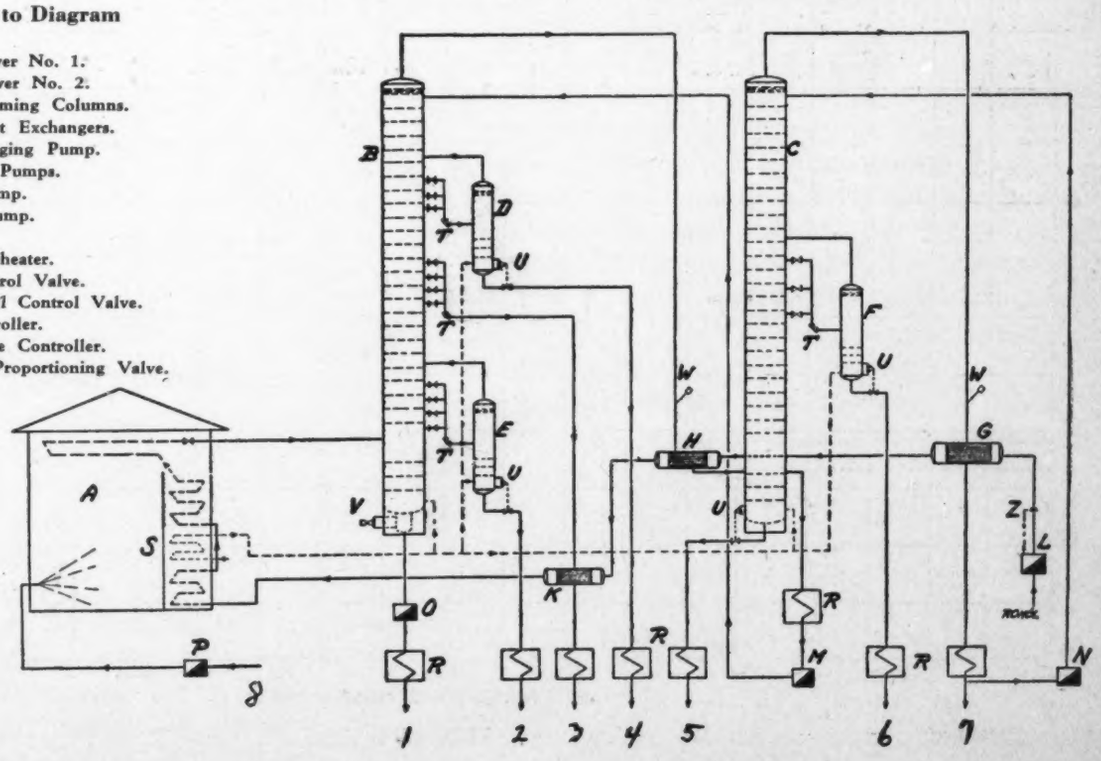
The asphalt produced is free from carbon and the benzole insoluble test on this product shows 0.05 per cent insoluble matter.

The plant is noted for its great efficiency in heat transfer, steam consumption, and for the purity of overhead cuts, and the arrangement described in this article is capable of giving sharper fractionation than do most of the modern pipe still arrangements.

Key to Diagram

A—Pipe still.
B—Bubble Tower No. 1.
C—Bubble Tower No. 2.
D, E, F,—Steaming Columns.
G, H, K—Heat Exchangers.
L—Crude Charging Pump.
M, N—Reflux Pumps.
O—Asphalt Pump.
P—Fuel Oil Pump.
R—Cooler.
S—Steam Superheater.
T—Outlet Control Valve.
U—Liquid Level Control Valve.
V—Level Controller.
W—Temperature Controller.
Z—Automatic Proportioning Valve.

1—Asphalt.
2—Heavy Par. Dist.
3—Light Par. Dist.
4—Gas Oil.
5—Kerosene.
6—White Spirit.
7—Motor Gasoline.
8—Fuel Oil.



Caustic Soda *and the* Petroleum Industry

[PART I]

L. J. CATLIN
Chief Chemist, Standard Oil Company of Kansas

CAUSTIC soda is manufactured into various forms to suit different trades, such as flake, ground, powdered, etc., but the only forms of particular interest to refiners are the solid form in drums, and the liquid form which is shipped in tank cars. The choice between these two forms is largely a question of freight costs, or where costs are nearly equal, a matter of convenience and economy in handling. Prices are of course based on actual content of sodium hydroxide in either case, although the prices are not the same per pound as the liquid can be produced cheaper than the solid, which is merely a completely dried product. The usual grades are for the solid about 98 to 100 per cent NaOH and for the liquid about 50 per cent NaOH. In connection with these designations, it may be pointed out that many of the manufacturers are adopting the practice of quoting the per cent NaOH instead of the per cent Na_2O which form of describing is a relic of the days of pure chemistry for chemistry's sake, and not for industrial processes. The rating most generally used was 76 per cent Na_2O which is equivalent

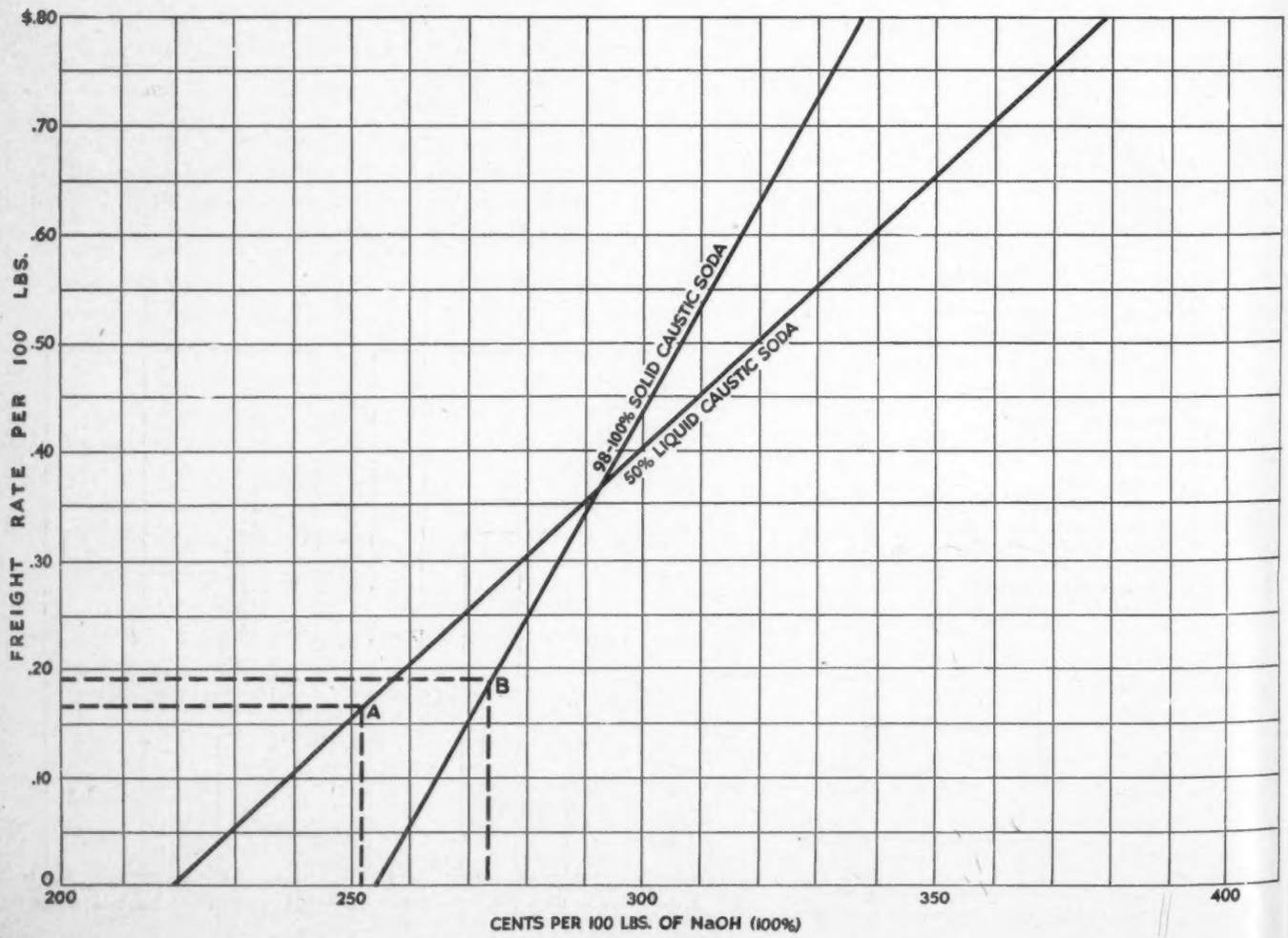


FIGURE I

to 98.09 per cent NaOH but the latter term is much more intelligible to the average person.

The economics of this question has been worked out on a graph by one of the marketers and is shown in Figure I. Comparison is given of the two forms, assuming a base price of $2.20 per 100 pounds for liquid and $2.54 per 100 pounds for the solid, with freight rates to be found on the other side of the chart. It is shown on this particular case that a freight rate of $.37 marks the critical point. If the freight rate is more than $.37 the total cost is less by using the solid form; if less than $.37 it is less for the liquid. For other base prices, lines may be drawn from the price line at zero freight rate, parallel to the respective lines for solid and liquid, and the new intersection will show the critical freight rate for that combination of prices.

In case the same freight rate does not apply to the solid and liquid, comparison may be made by starting on the freight line at the rate, and following horizontal to the line which bears that rate, then reading total cost vertically below, as illustrated by dotted lines for a rate of $.16½ for liquid and $.19 for solid, resulting in total cost of $2.51 for liquid and $2.73 for solid.

Assuming a case in which the total cost is equal, there are a number of factors entering into consideration of which to use. In the first place consideration must be given to equipment for handling. Solid caustic is shipped in drums sealed with friction caps and weighing in the neighborhood of 700 pounds per drum. Greatest convenience in this case comes from car lot shipments where an industrial siding is located near the treating plant or other principal point of use, and platforms or inclines can be installed for rolling drums directly to place of storage and use. Where hauling is necessary it is usual practice to erect platforms or other structures for storage on a level with truck beds to avoid lifting. Convenient supports are often built of angle iron with the channel turned up to act as guides for the drums. Such a system for storage and handling was described in The Refiner and Natural Gasoline Manufacturer, Vol. 11, No. 1, Jan. 1932, page 40. If melting tanks are placed at one end of such storage platform no further lifting is necessary. Sheltered storage is not absolutely necessary for caustic drums, but is often provided where shipments are considerable in advance of use.

Solid caustic soda is usually removed from drums by melting with a jet of open steam directed into the opening provided by removing the friction cap, and punching a few holes near the edge to allow the melted caustic to drip out. A tank must be provided large enough to allow sufficient dilution to prevent solidifying again after removal from the drums. From this point handling will be the same as with liquid caustic.

Essential equipment for handling liquid caustic soda consists of (1) tanks for storage; two tanks of at least 10,000 gallons capacity should be sufficient in most cases. (2) Pipe lines from unloading point to storage

"THE Earning Power of Research," was an expression frequently seen in technical and industrial papers in the years following the war. Dramatized by war, and popularized by a group of chemists who knew the language of business and luncheon clubs as well as the college lecture room, this slogan has thoroughly permeated the thought of executive offices through the country and fired the imagination of youth in the schools until we need not fear that America ever will lag behind the rest of the world in scientific development.

What will be the next slogan is a question that might help to answer many anxious queries today. It is being coined at present but it will be not merely some clever quip but something which expresses the answer to the fix we are in. We know it is due because the world thinks only in short hitches and when something gives the world a jolt it has to start over. For a long time we had what was called Twentieth Century Conditions; then we had post-war conditions; now we are entering post-depression conditions. But they have not been "posted" yet.

This is not intended to convey the impression that the importance of research has diminished. As a chemist I do not intend to leave the impression that the importance of chemistry to industry ever will do other than increase. But research has been more carefully defined in the minds of the executives as well as the chemists until research is in many instances a department unto itself with programs far beyond individual effort.

Some have never abandoned the hope of making some "great discovery" but many realize that nothing will come of discovery unless it is tied into some larger plan. Even the once simple matter of taking out a patent has gone beyond the reach of an individual in a lifetime and the usefulness of most patents is exhausted before the papers can be issued. So the best job for the chemist may be that of swapping stories and improving the "art" of chemistry, which is in other words showing the "earning power of chemical control."

Reviewing fundamentals is always profitable and outside contacts stimulate fresh thought. My only regret is that the editor did not assign this subject to someone in the cuastic soda industry as was done with Lime recently discussed by S. P. Armsby. In attempting to cover this subject I have had helpful cooperation from manufacturers and marketers of caustic soda.

The Author.

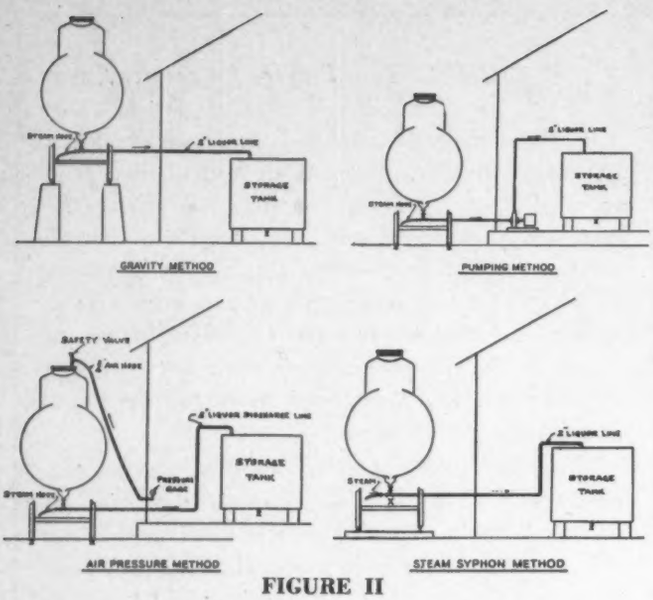


FIGURE II

and from storage to point of use; (3) steam line at the car unloading point for winter unloading; (4) means of transferring liquid, either centrifugal pump or air-pressure.

Storage tanks should either be in buildings where heat is available, or insulated and provided with heating coils for winter use. Temperatures above 55° F. will prevent any trouble from crystallizing of the 50 per cent solution. Details of handling from tank cars may be suggested by Figure II.

In connection with handling of liquid caustic soda there might be a case in which sufficient storage space is available to allow diluting as it is unloaded to obviate the necessity of warm storage rooms. Figure III affords information necessary to calculate the amount of dilution necessary to prevent freezing, or crystallizing at temperatures anticipated. The lower, irregular curve, shows crystallizing, or freezing points for various strengths, and the upper curve boiling points. The lower curve finds application to handling problems with either type of caustic and also suggests that there may be differences in chemical properties for certain uses due to differences in molecular structures.

When working with or near caustic soda in any form, care should be taken to prevent this chemical from getting on to the clothing or body. Cotton, linen and rubber are more resistant to caustic soda than leather or wool which are easily attacked. Rubber gloves are excellent protection for the hands but have a tendency to become slippery and on this account are disagreeable to use. Heavy canvas gloves offer excellent protection which is still further improved by placing an additional piece of heavy canvas cloth over the palms. Canvas shoes with rubber soles and heels are quite satisfactory although some workmen prefer low acid-proof rubber shoes. Glasses or goggles should be worn at all times when handling caustic soda.

Caustic soda coming in contact with the skin tends to penetrate into the flesh tissues rapidly, producing bad burns unless prompt action is taken. Whenever this occurs, a 10 per cent solution of amonium chloride should be applied freely to the parts affected. If caustic soda comes in contact with the eyes, a one per cent solution of ammonium chloride or a two per cent solution of boric acid should be used immediately as an eye wash. It is highly advisable, therefore, to maintain a source of water and a first aid cabinet, conveniently located near workmen handling caustic soda. The cabinet should contain the solutions mentioned above and also an eye glass, a tumbler and a wash bottle of water. All caustic burns should receive prompt and competent medical attention immediately following first aid treatment.

Most refineries have safety organizations which assure fairly intelligent handling of such cases, but in case workmen are sent to first aid stations for treatment care must be exercised to see that those in charge know what the nature of chemical burns are. This is necessary because of the tendency of men unfamiliar with chemicals calling everything "acids." The writer recalls one such case in which a pipe fitter came in for treatment for "acid" burns and after thoroughly treating with sodium bicarbonate and putting on the ointments, it was discovered that the burns were caustic burns which should have received the opposite treatment.

ACKNOWLEDGMENTS

We wish to express our appreciation to the following companies for cooperation and information in preparing these articles: Solvay Sales Corporation; Columbia Alkali Corporation; Mathieson Alkali Works, Inc.; and Diamond Alkali Company.

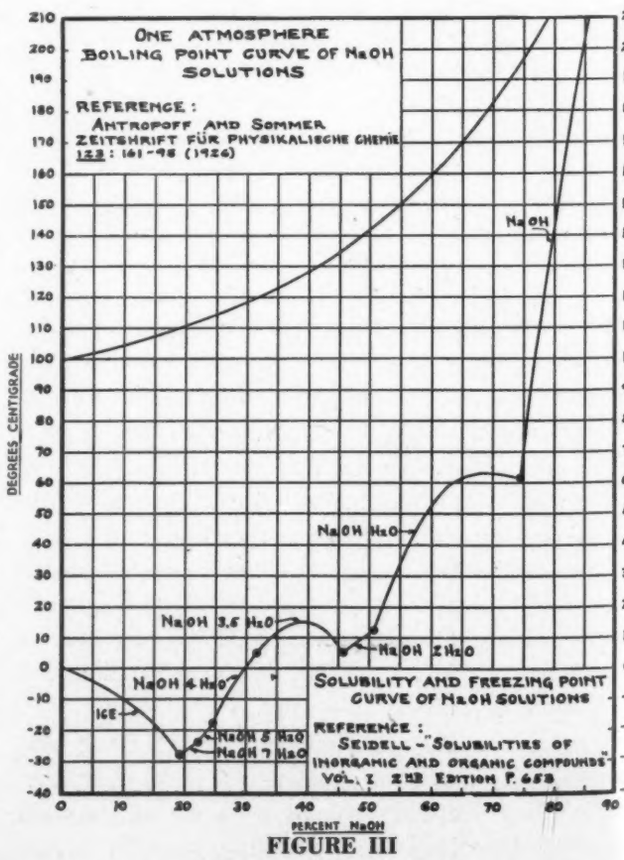


FIGURE III

Hydrogenation Now Proven Development at Bayway

Process operated more than two years and products are ready for the market

GEORGE REID
Associate Editor

STANDARD Oil Company of New Jersey was host to a group of 48 representatives of various engineering societies, companies and members of the scientific press and 39 representatives of the company and affiliated concerns, Tuesday, August 9, at its twin installation of the hydrogenation process on the yard of the Bayway, New Jersey, refinery.

Meeting at New York headquarters, the visitors were taken to the plant by private boat, at which time luncheon was served and literature descriptive of the hydrogenation system was presented each member of the group. At the plant the visitors were arranged in groups of about eight, each group provided with a guide, and shown through the various steps of the process.

Visitors were first taken through the plant for manufacturing hydrogen from hydrocarbon gases and shown how this material is prepared and purified, then through the compression stage where pressures of 3600 pounds are reached. They were shown how the hydrogen and the oil are mixed, the heaters for securing operating temperatures, the stalls housing the catalytic chambers, the various instruments of control and regulation, and the accumulation of the finished product—at this time lubricating oil.

Questions as to operating procedure, information as to equipment, its operation, maintenance and its lasting qualities under such severe conditions, were freely answered.

After two years of operation these units are still in excellent condition and there appears no reason why they should not operate as successfully for a like period in the future. The practicability of hydrogenation has been well illustrated at Bayway and it appears that the company never seriously doubted its commercial practicability, for the first units have been placed in such manner that several more units may be erected on the same site and it is possible that this expansion of facilities may be brought about in the not far distant future.

More will be heard of hydrogenation. The difficulties of the early or "exploratory" days have all been solved. The units operate with the same smoothness of ordinary refining processes. The process itself is not a thing of mystery, and its construction and operation is simple. With operating pressures of 3600 pounds a natural hazard exists, but every possible safeguard is successfully provided.

After an afternoon of visiting the group was returned to New York by boat.

The following description of the plant was released by the company.

THE hydrogenation plant at Bayway really consists of two units, each housed in a separate concrete stall. Each unit has a daily charging capacity of from 2500 to 5000 barrels, depending upon the type of charging stock and the products being manufactured.

In the production of "Essolube" (a new motor oil which has been developed under the hydrogenation process and which is now ready for the public) the capacity ranges from 2500 to 3500 barrels a day, varying with the charging stock. When making anti-knock gasoline it is possible to attain a total feed charging capacity in the neighborhood of 5000 barrels a day.

The manufacture of hydrogenated lubricating oils is largely a liquid phase operation, the oil being charged into the reaction towers in the liquid form at a temperature approximating 800°F. Production of anti-knock gasoline, on the other hand, takes place in the vapor phase at a temperature around 1000°F.

HOW HYDROGEN IS OBTAINED

Hydrogen may, of course, be made in more than one method. At Bayway hydrogen for the process is derived from cracking coil gas. At the present time about 2,000,000 cubic feet are manufactured every day, although the plant can generate from 6,500,000 to 7,000,000 cubic feet a day.

The cracking coil gas first receives a preliminary

At left—The first published picture taken inside the stalls. Behind the seven-inch alloy steel walls of these 40-foot towers hydrogen and oil at 3600 pounds pressure and 750 to 1000 degrees temperature are being forced through the packed catalyst. Molecules of the oil are literally torn apart here and reformed according to product specifications.

On opposite page — A picture of the massive concrete stalls which enclose the heavy steel reaction chambers where hydrogenation actually takes place. Notice the 150-ton electric crane, used for removing the reaction towers when necessary.

scrubbing at the gasoline recovery plant located in the refinery proper. Then it is treated in a Koppers system and caustic washer for removal of sulphur constituents. Then it is ready for the reforming furnaces.

Here the purified refinery gas, mixed with steam, passes through tubes packed with catalyst and heated to a temperature of about 1800°F. with a pressure of approximately 15 pounds per square inch. Through the reaction of the hydrocarbons in the gas with the steam a mixture of hydrogen and carbon monoxide is produced. The following chemical reaction may be taken as typical of this step:

$$CH_4 + H_2O = 3H_2 + CO$$

The heat from the flue gas coming from the reforming furnaces is utilized in the production of process steam by means of a waste heat boiler. With this installation it is possible to make about one half of all the steam required in the process.

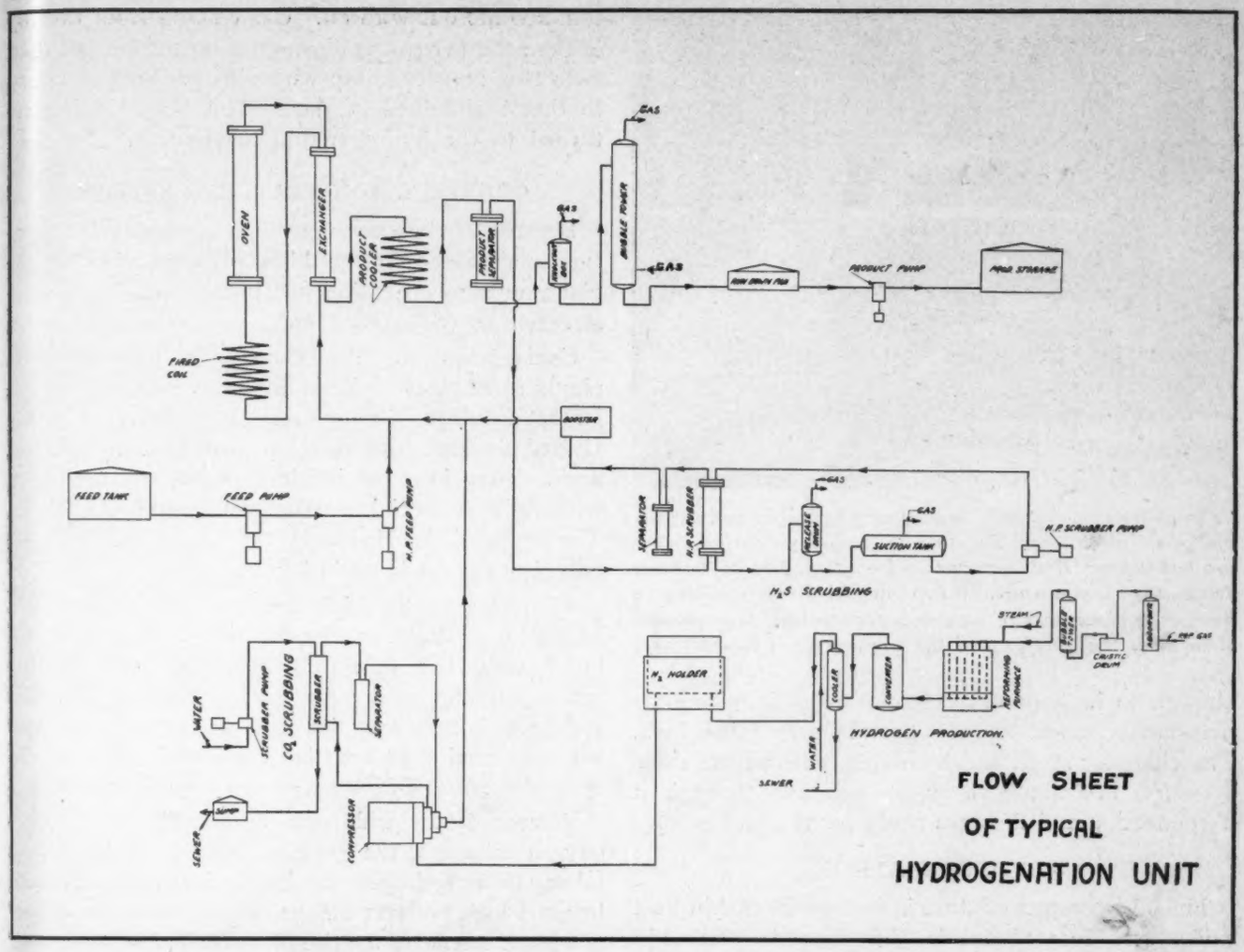
Still more steam is added to the hydrogen-CO mixture leaving the furnaces, and in the second phase of the process, known as conversion, hydrogen and carbon dioxide are made. The gases pass up through catalyst-filled trays in a tower which is maintained at a temperature of about 850°F.

The equation here is

$$CO + H_2O = CO_2 + H_2$$

The gaseous mixture leaving the converter is composed of about 79 per cent hydrogen, 20 per cent carbon dioxide and one per cent unconverted hydrocarbons and other gases.

The gases are cooled by passing counter-currently



to water in a coke-packed cooling tower. The cooling water is circulated through an atmospheric cooler and then re-cycled. From the cooler the gases are led to hydrogen gas holders, where they are stored until needed.

The gaseous mixture is taken from the holder through a moisture trap and introduced into the compressor system.

WORKING UP THE PRESSURE

There are three electric and two steam-driven units in the compressor house. In four stages the gas is raised to the hydrogenating pressure of 3600 pounds per square inch. But between the second and third stages it must be stripped of its CO_2 content.

This is done by passing the gaseous mixture through a packed scrubbing tower counter-current to sea water at a pressure of 240 pounds per square inch. This pressure causes the carbon dioxide to dissolve in the water and reduces the CO_2 content of the gas from about 20 per cent to less than 0.6 per cent. It then goes to the third and fourth stages to be compressed to the hydrogenating pressure.

Gas is supplied by the compressor system to the hydrogenating equipment at the rate necessary to maintain the desired reaction pressure.

The feed stock to be hydrogenated is pumped from

"The police department." Individually hydrogen and oxygen are peaceful citizens. Together in proper proportions they are bad actors. Hydrogen is tested continuously as it comes from the compressors. When anything approaching a dangerous percentage of oxygen is approached, an automatic siren gives the warning and the compressor is closed down.

storage to high pressure feed pumps, in which its pressure is raised to 3600 pounds per square inch. The charging stock and hydrogen, both at the same pressure, are finally brought together through a T-connection and then are ready for the final step.

HYDROGENATION

The oil-hydrogen mixture is first pre-heated in heat exchangers located inside the concrete stalls, in which they pass counter-current to the hot hydrogenated products coming from the reaction chambers. The oil-gas mixture is then raised to the reaction temperature in a gas-fired coil quite similar to the conventional tube heaters.

In the reaction chambers, of which there are four in each unit, the mixture passes upward through the packed catalyst at the hydrogenating temperature and pressure—this varying, as was already explained, with the feed stock and products desired—which causes the oil and some of the hydrogen to unite. The reaction is exothermic, so that a relatively small amount of heat need be supplied by the fired coil.

The reaction products pass out the top of the chambers and are led through the heat exchangers and a cooler to a release drum. Here the gas and liquid are separated, the liquid being released into a low-pressure separator maintained at a pressure of around 200 pounds per square inch. Any gas remaining at this stage is drawn off and sent to the burning line, while the liquid products are scrubbed to remove hydrogen sulphide and pumped to storage.

Gases coming from the high pressure release drum are led to an oil scrubber before being re-circulated. Hydrogen has a tendency to become contaminated with unconverted hydrocarbons in the process, and so it is necessary from time to time to wash these constituents out with oil. Gas coming from the top of the scrubber passes through a separator, and then goes to a booster pump where its pressure is raised to that maintained in the system before being returned to the hydrogenating equipment.

CONSTRUCTION FEATURES, SAFETY

Because of the extremely high operating temperature maintained in the high pressure side of the plant, unusual attention has been given in its construction to the safety factor.

Construction of the company's hydrogenation plants at Bayway and Baton Rouge necessitated the largest forgings of alloy steel ever fabricated in the United States. The reaction chambers are 40 feet high. They have an inside diameter of three feet, with walls of special construction seven inches thick. The walls of the chambers are not of one material only, but are made up in layers.

All piping in the high pressure side of the plant is of unusual thickness. Leak-proof joints are effected by drawing two accurately machined ends together against an alloy steel gasket. Machining of pipe ends and liners is so precise that even when the flange bolts are only hand tightened the joints will withstand the system pressure of 3600 pounds per square inch.

Because of the wide explosive range of hydrogen-oxygen mixtures, the greatest precautions have been taken. The hydrogen gas holder is fitted with both low and high pressure alarms, which sound in the control room whenever the rise of the holder becomes such that there is likelihood of an escape of hydrogen into the atmosphere, or of inward leakage of atmospheric oxygen.

The oxygen content of the gas on the high pressure side of the plant is maintained at less than 0.2 per cent by means of a special recorder-alarm device, which is attached to the compressor discharge line. A small but representative sample of the gas is continuously removed from the line and passed through the recorder-alarm.

In this instrument the gas is washed and dried and passed through electrically heated porcelain tubes containing a platinum-black catalyst. The tubes are heated to a temperature of about 300° F., at which temperature and in the presence of this catalyst, any oxygen present reacts with the hydrogen to form water. This reaction is highly exothermic. An accurate thermocouple pyrometer records the temperature in the furnace and any increase in temperature due to the formation of water is immediately recorded on a scale graduated in per cent of oxygen. The electrical energy generated in the thermocouple by the heat of reaction actuates an electric alarm, which sounds in the control house. Whenever the oxygen content of the gas rises above 0.2 per cent maximum, the high pressure equipment concerned is immediately shut down and the cause of the trouble investigated.

A Thumb-Nail Sketch of the Hydrogenation Process

THE history of hydrogenation as developed today goes back before 1912. The work was started by a Dr. Haber and was perfected by Dr. Bosch of Heidelberg, Germany. It was found that by combining hydrogen under certain conditions with nitrogen from the air, nitrates for the manufacture of fertilizers and explosives at least equal to the natural product then imported from Chile, could be produced. About the same time another German, Dr. Bergius, was bending his efforts toward combining hydrogen and coal by much the same methods to form liquid hydrocarbons such as gasoline and oil.

Hydrogenation came near to winning the war for Germany. While the Allies were busy blockading her against nitrate shipments from Chile, which meant life for her big guns, Germany was literally plucking explosives and fertilizers from thin air. When peace came the process was carried on by the I. G. Farbenindustrie Aktiengesellschaft. In 1926 developments had progressed sufficiently to attract the attention of the Standard Oil Company of New Jersey, and the following year the company signed an agreement with the I. G. for mutual development of the process. A 100-barrel experimental plant was built at Baton Rouge, Louisiana, and for two years the company's scientists worked on the problem of applying the process to petroleum.

In 1929 construction was started on the first plant especially built for oil hydrogenation at Bayway, New Jersey. This was followed by a similar plant at Baton Rouge. For two years products were turned out under commercial operating conditions and innumerable tests run to determine their cost and how they might be improved. Now, at the end of two years, hydrogenated products are ready to go on the market.

Control and operation of the hydrogenation process throughout the world is apportioned among the following companies, in the manner described:

I. G. Farbenindustrie, A. G.—for Germany

Standard-I. G. Company—stock owned jointly by Standard Oil Company of New Jersey and I. G. Farbenindustrie, with the former having the controlling interest. Receives all royalties on the process for the world outside of Germany.

International Hydrogenation Patents Company—controls all patents on the process for the world outside the United States and Germany, paying royalties to Standard-I. G.

International Hydro Engineering and Chemical Company—acts as expert consultant on engineering and chemical problems connected with the process for the world outside the United States and Germany. Also acts as agent for International Hydrogenation Patents Company.

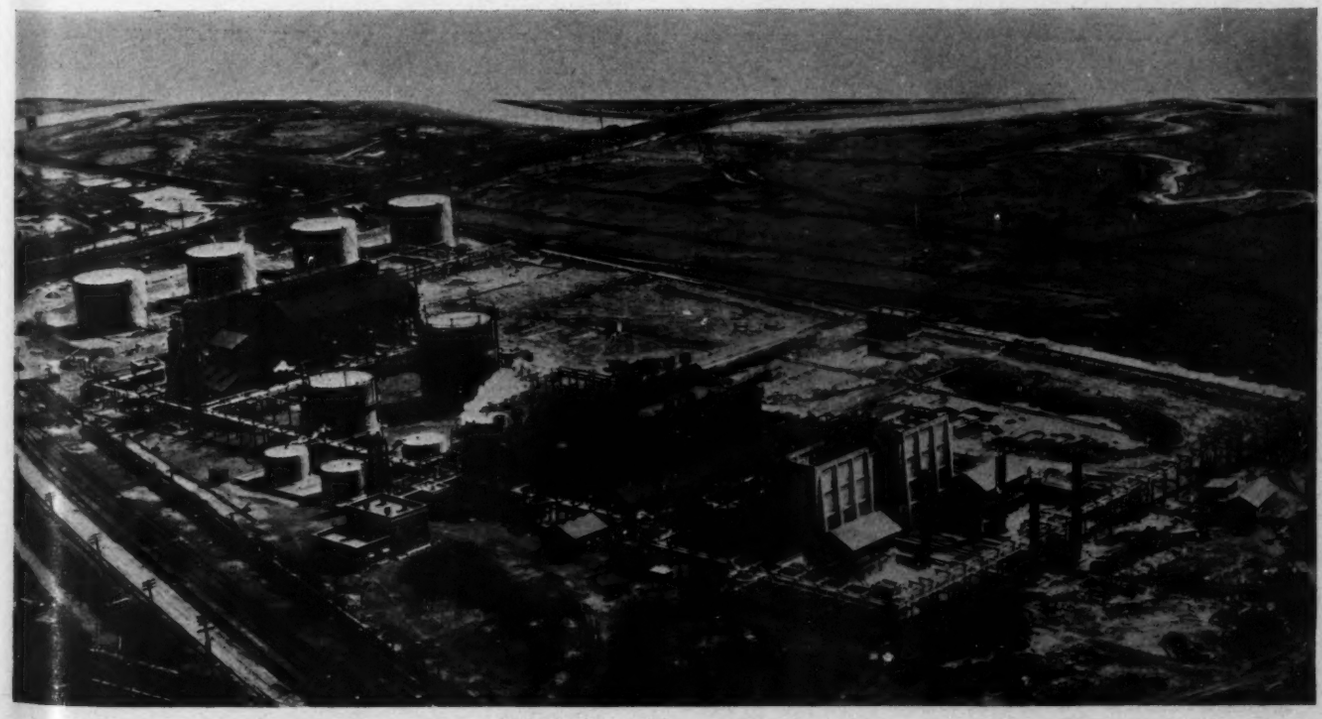
Hydro Patents Company—controls all hydrogenation patents in the United States. Stock of this company was offered to all oil refiners of sufficient size to make them potential users of the process, and was accepted by more than 90 per cent of such companies.

Companies holding stock in Hydro Patents as of July 1, 1932, are as follows:

Atlantic Refining Company
Barnsdall Corporation
Consolidated Oil Company (Sinclair Refining Company)
Continental Oil Company
Mid-Continent Petroleum Corporation
The Pure Oil Company
Richfield Oil Company of California
Shell Union Oil Corporation
Skelly Oil Company
Socony-Vacuum Corporation
Standard Oil Company of California
Standard Oil Company (Indiana)
Standard Oil Company (Ohio)
Standard Oil Development Company (for Standard Oil Company (New Jersey) interests)
The Texas Company.

Hydro Patents Company pays royalties on the process to Standard I. G.

Hydro Engineering & Chemical Company—acts as expert consultant on engineering and chemical problems connected with the process in the United States.



Concrete stalls at the right are where the hydrogenation reaction takes place

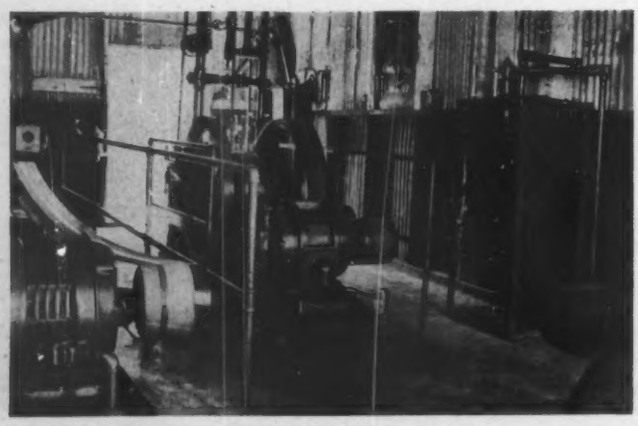
Simple Vapor Recovery Plant . . . *for* Topping Refinery

DOING no cracking, and therefore having a small amount of recoverable vapors from the look boxes and storage, Dale Oil & Refining Company could not see the financial advantage in installing an elaborate vapor recovery plant in its Refinery at Electra, Texas.

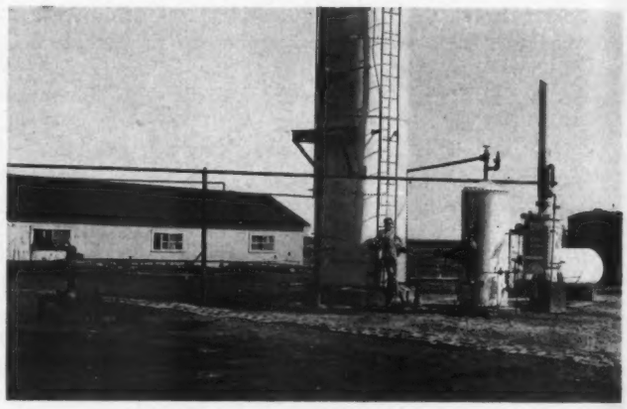
Utilizing practically all the equipment encorporated in the small plant from tankage and pumps found idle in the yard, officials have built a small layout that does the work quite satisfactorily.

In the first place, they had a Sullivan 9 by 10 compressor which was placed on the idle material list when the agitators were discarded in favor of continuous closed treating of gasoline and kerosene. Rigging this up with a short belt drive to a General Electric Type Kt512 20 horsepower 220 volt motor, it was placed in the vacuum lines laid to the look boxes and to the storage tanks in which the crude was stored. Lines were also laid to the run-down tanks and to gasoline storage, together with lines leading to the rack to remove the vapors created when blending with natural.

A Southwestern enclosed cooler used to cool the gas from the discharge of the compressor, was installed in the yard near the run-down tanks. A small accumulator was set on the outlet of this cooler to retain the gasoline condensed in it. Setting a tower five by 25 feet to act as an absorber, trays were placed in it.



Vapor Recovery Compressor



Vapor Recovery Plant

A combination batch and circulation method of absorption is obtained in this tower. Gasoline of a high initial and low gravity is placed in one of the two six by 30 storage tanks, which is pumped from there to the tower. The vapors are picked up from the various points through a Fulton duplex super sensitive regulator, maintaining a pressure of four-inch vacuum on the lines leading to the points of recovery. The gas is discharged into the absorber where a close check is made periodically on the gravity of the gasoline in it. When a pronounced rise is found, the material is pumped back into the other tank while a fresh charge is placed in the absorber.

Recovering approximately 800 gallons of gasoline per day by this method, which does not require an extra man to operate, has been found to be well worth the money expended. While not as efficient as a more elaborate system of continuous circulation with a fractionator, the plant is stripping the vapors. After these leave the absorber, they are directed to the burners in the boiler room and to stoves in the house row and office.

Except for the time that the chemist gives the plant in checking the condition of the absorption medium, George Jennings, superintendent, says that it has not added to the expense of his operation.

Acid Treatment of

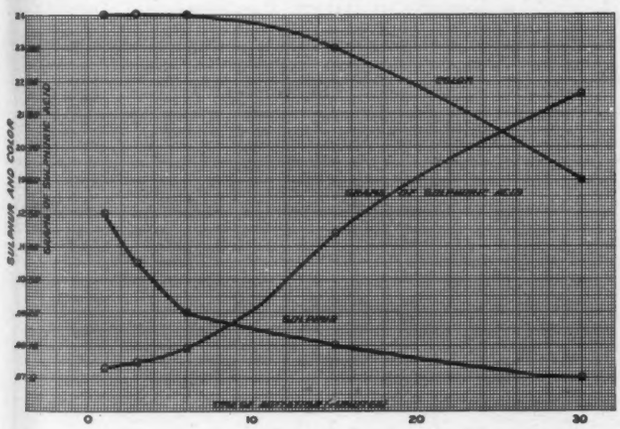
Cracked Distillate

INVOLVES MANY FACTORS

A. W. TRUSTY
Louisiana Oil Refining Corporation

CRACKED distillate is treated with sulphuric acid to reduce the gum, lower the sulphur content and to improve the color and odor. In some cases where the sulphur content, for instance, is low, the improvement of color and the removal of gum is more important. In other cases where the sulphur content is high and where a good color can be obtained with a small amount of acid, the reduction in sulphur content is more important. The various factors of time of contact, temperature of treatment, time of settling before neutralization with caustic, strength of caustic for neutralization, etc., have been systematically investigated, and a study has been made of the effect of the various factors on the color, sulphur, and acidity of the rerun overhead.

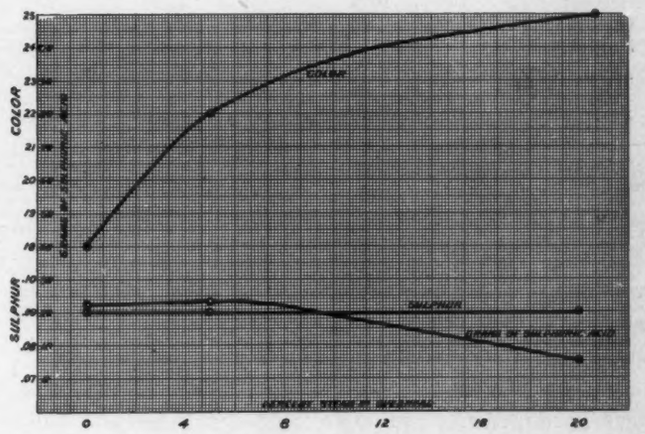
When gasoline or kerosene containing unsaturated hydrocarbons is refined by sulphuric acid and redistilled, liberation of sulphur dioxide is nearly always noted. The sulphur dioxide combines with the water condensed from the steam or with free water present in the feed stock. Sulphurous acid, and, in nearly every case, small amounts of sulphuric acid results,



I

EFFECT OF TIME OF AGITATION

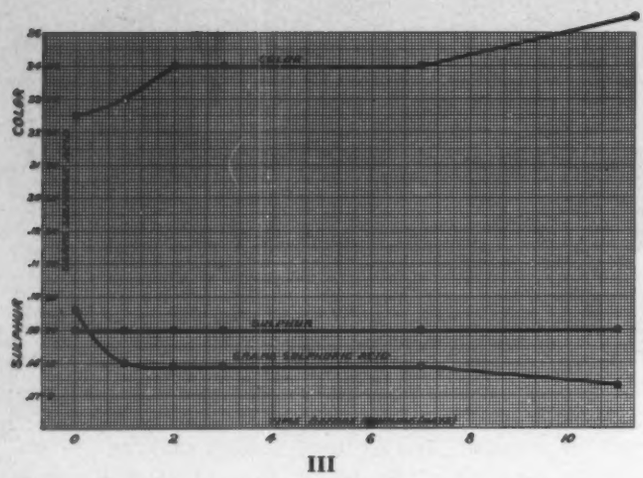
	A	B	C	D	E
Amt. of oil c.c.	1000	1000	1000	1000	1000
Lbs. acid/bbl. oil	10	10	10	10	10
Time of agitation (min.)	1	3	6	15	30
Time of settling (min.)	5	5	5	5	5
Time of caustic wash (minutes)	1	1	1	1	1
Time before rerunning	1 day	1 day	1 day	1 day	1 day
Amount of oil rerun	800	800	800	800	800
% overhead	84	84	84	84	84
% steam	6	6	6	6	6
Tests on Overhead—					
Gravity	54.5	54.4	54.5	54.2	54.4
I. B. P.	126	128	132	125	128
% 158	4.5	3.5	4	3.5	3.5
% 212	21	18	20	18	17.5
% 221	21.5	21	22	20.5	20
% 284	48	48	49	47.5	48
% 392	93.5	94	94	94	94
End Point	410	411	410	410	409
Recovery	98	98	98	97.5	97.5
Color	25	25	25	23	19
Sulphur	0.12	0.105	0.09	0.08	0.07
Grams sulphuric acid/bbl.	3.1	5.1	9.2	43.5	86



II

EFFECT OF AMOUNT OF STEAM USED IN DISTILLATION

Lbs. acid/bbl.	10	10	10
Time of agitation (min.)	6	6	6
Time of settling (min.)	5	5	5
Per cent steam in overhead	None	5%	20%
Time before rerunning	1 day	1 day	1 day
Tests on Overhead—			
Gravity	54.0	54.4	54.2
I. B. P.	126	126	126
% 158	3.5	4	3.5
% 212	17.5	18	18
% 221	20.5	21	21
% 284	43.5	46	45.5
% 392	91	92	92
End Point	406	408	409
Recovery	97	97	97
Color	18	22	25
Sulphur	0.09	0.09	0.09
Acid in Overhead Grams H_2SO_4/bbl. oil.	22.2	23.2	5



III

EFFECT OF STORAGE TIME BEFORE RERUNNING

Lbs. acid/barrel	10	10	10	10	10	
Tiime of agitation.....	6	6	6	6	6	
Time of settling.....	5	5	5	5	5	
Time before rerunning.	Rerun at once	1*	2*	3*	7*	11*
% steam used	6	6	6	6	6	6
Tests on Overhead—						
Gravity	54.2	54.5	54.3	54.1	53.6	54.2
I. B. P. 128		125	126	125	124	125
% 158	3.5	4	3.5	4.5	4	3.5
% 212	17	18.5	18	17	..	17
% 221	20	21.5	21	20.5	20	20
% 284	45	46	44	46	45	45
% 392	93	94	93.5	92	92	92
End Point 409		410	411	408	410	411
Recovery	97.5	97.5	97.5	97.5	97.5	97.5
Color	22+	23	24	24	24	25+
Sulphur	0.09	0.09	.09	0.09	0.09	0.09
Acid in overhead:						
Grams H_2SO_4/barrel oil	26.2	10.2	9	9.1	9.1	3.5

* Days.

which gives the overhead naphtha and water an acid reaction. This acidity causes a loss in color of the rerun naphtha in some cases before the naphtha can be pumped to the treating and blending tanks. The color stability of the finished gasoline is also impaired by the action of this weak acidity. Corrosion of the stills, towers, condensing equipment, rundown lines and tanks also results from this acidity, the degree of corrosion depending on the amount of acidity, the temperature, and the amount of oxygen present. Incidentally, a good way to check the amount of corrosion is to determine by chemical analysis the amount of iron in the rundown water. With the volume of water and the amount of iron, known, the rate rate of corrosion can be calculated. With these considerations, it is evident that it is very important to investigate the means of reducing the formation of acidity at the rerun stills.

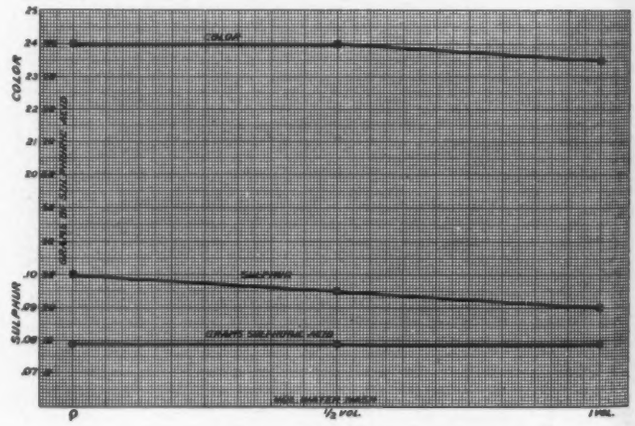
A large sample of cracked distillate made from cracking a mixture of Smackover crude and Winkler County crude residue under 300 pounds pressure and 900°F. coil outlet temperature was secured for all treats. 1000 c.c. portions of distillate were treated in a 2000 c.c. agitator by hand treatment. The same person made all agitations in order that the treats might be more uniform. All treats were agitated for five minutes, and allowed to settle for five minutes before caustic neutralization. All treats were allowed to stand for 24 hours before rerunning. Electric heaters were used as a source of heat for the rerunning operation in order to maintain a uniform rate of distillation.

The acidity of the rerun overhead was measured by passing the overhead into an excess of standard sodium carbonate solution for neutralization. After the distillation the aqueous layer was back-titrated with standard hydrochloric acid solution, which, by calculation gave the amount of acidity formed in the distillation process.

CONCLUSIONS

I. Effect of Time of Agitation During Acid Treatment.
   1. The longer the time of agitation, the greater the reduction of sulphur.
   2. Too long agitation gives a poor color on the rerun gasoline.
   3. The longer the agitation, the greater the amount of acid formed at rerun stills.

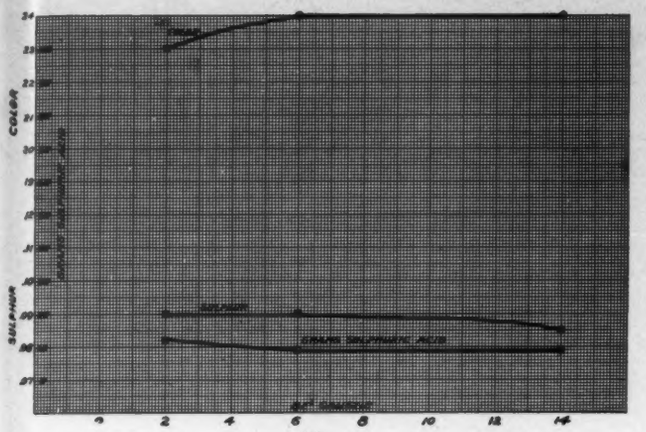
II. Effect of Amount of Steam used in Distillation.
   1. The more steam used the better the color on the rerun overhead.
   2. The amount of steam has very little effect on the sulphur content of the rerun overhead.
   3. An increase in steam decreases the amount of acid formation at the rerun stills.



IV

EFFECT OF WATER WASH

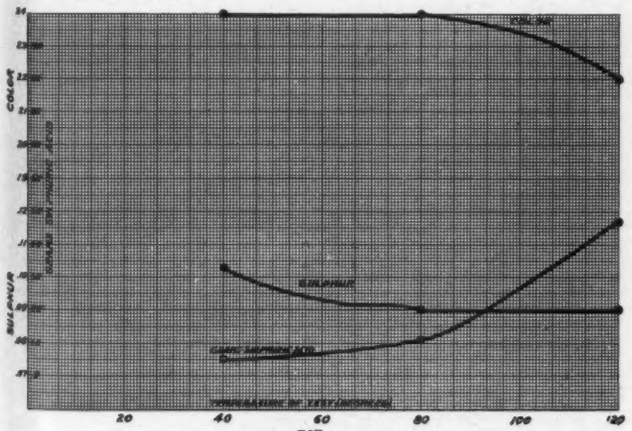
Lbs: acid	10	10	10
Time of agitation.....	5	5	5
Time of settling.....	5	5	5
Remarks . .....No water wash		½ vol. water wash	1 vol. water wash
Time before rerunning.	1 day	1 day	1 day
% steam used	6	6	6
Tests on overhead—			
Gravity	54.0	54.5	54.0
I. B. P.	126	128	122
% 158	4	3.5	3.5
% 212	17	18	17
% 221	20.5	22	21.5
% 284	46	46.5	48
% 392	93	94	93
End Point	408	410	409
Recovery	98	98	97.5
Color	24	24	23+
Sulphur	0.10	0.095	0.09
% acid in overhead—			
Grams H_2SO_4/bbl oil	9	9	9



V

EFFECT OF CAUSTIC WASHES

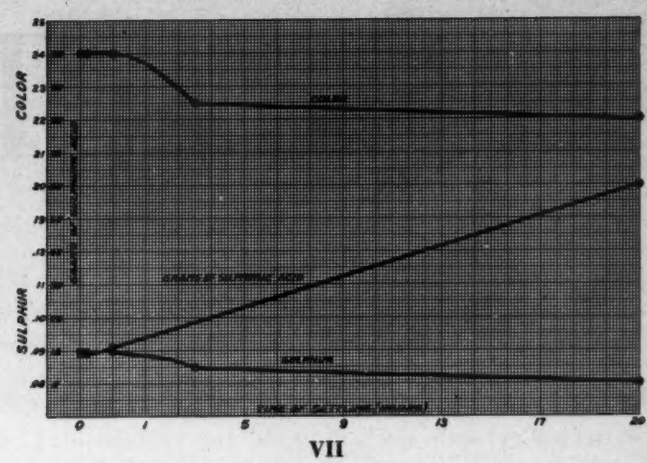
Lbs. acid/bbl.	10	10	10
Time of agitation	6	6	6
Time of settling	5	5	5
Neutralized with	2 Be. Caustic	6 Be. Caustic	14 Be. Caustic
Time before rerunning	1 day	1 day	1 day
% steam in overhead..	6	6	6
Tests on overhead—			
Gravity	54.1	54.3	54.3
I. B. P.	132	127	126
% 158	3	3	3.5
% 212	16	17.5	17
% 221	19.5	21	20
% 284	45.5	46.4	46
% 392	93	93	92.5
End Point	408	407	409
Recovery	97.5	97.5	97.5
Color	23	24	24
Sulphur	0.09	0.09	0.085
% acid in overhead—			
Grams H_2SO_4/bbl oil	12	9	9



VI

EFFECT OF TEMPERATURE DURING ACID TREATMENT

Lbs. acid/bbl.	10	10	10
Time of agitation	5	5	5
Time of settling	5	5	5
Temperature of test..	40°F.	80°F.	120°F.
Time before rerunning	1 day	1 day	1 day
% steam in overhead..	6	6	6
Tests on overhead—			
Gravity	53.4	53.4	54.2
I. B. P.	126	125	124
% 158	3	3	3
% 212	17	17	17
% 221	20	19.5	21
% 284	45.5	44	46
% 392	92	91.5	93.5
End Point	410	407	409
Recovery	97.5	97.5	97.5
Color	24	24	22+
% acid in overhead—			
Grams acid/bbl. oil.	5	11	47
Sulphur	0.103	0.09	0.09



VII

EFFECT OF SETTLING TIME BEFORE CAUSTIC NEUTRALIZATION

Lbs. acid/bbl.	10	10	10	10	10
Time of agitation (min.)	6	6	6	6	6
Time of agitation (min.) ..	No settle	5	30	3 hrs.	20 hrs.
Time before rerunning	1 day	1 day	1 day	1 day	1 day
% steam used	6	6	6	6	6
Tests on overhead—					
Gravity	54.3	54.4	54.1	54.1	54
I. B. P.	127	126	128	132	122
% 158	3	3	3	3	3
% 212	17	16.5	17.5	16	17
% 221	20	20	20.5	19	20.5
% 284	45	45.5	46.5	45	46
% 392	93	92.5	93	92	93
End Point	410	407	409	408	410
Recovery	97.5	97.5	97.5	97.5	98
Color	24	24	24	22+	22
Sulphur	0.09	0.09	0.09	0.085	0.08
Acid in overhead—					
Grams H_2SO_4/bbl oil	9	9	11	54	60.1

III. Effect of Storage Time Before Rerunning.

1. A storage time of one day or more before rerunning improves the color on the rerun gasoline.
2. Sulphur content is not affected by storage.
3. Storage time before rerunning reduces formation of acid at the rerun stills.

IV. Effect of Water Wash Before Caustic Neutralization.

1. A water wash before caustic neutralization does not affect the acid formation at the rerun stills.
2. A water wash lowers the sulphur content slightly on the rerun gasoline.
3. A water wash does not affect the color of the rerun gasoline.

V. Effect of Caustic Wash.

1. A caustic strength higher than 2 Be is preferable. However, any strength above 4 Be will give the same results at the rerun stills on sulphur, color and acid formation.

VI. Effect of Temperature of Acid Treatment.

1. A low temperature treatment gives the same color as a high temperature treatment.
2. The acid formation at the rerun stills is markedly less on the distillate treated at a low temperature than on the distillate treated at a high temperature.
3. The sulphur is slightly lower on the distillate treated at a high temperature.

VII. Effect of Settling Time.

1. Prolonged settling time before caustic neutralization *markedly* increases the acid formation at the rerun stills.
2. Prolonged settling time tends to affect the color on the rerun overhead.
3. Prolonged settling time lowers the sulphur slightly on the rerun gasoline.

...How To Baffle Boilers

W. F. SCHAPHORST, M. E.

IN securing better efficiency or more economical operation of the steam generation plant it is often only necessary to improve the baffling of the boilers in accord with modern design. When there is dissatisfaction with prevailing boiler installations it may not be necessary to scrap them and install new ones, for very often the same results can be obtained by improving or modernizing the baffling of the old boilers. Figures 1, 3, and 5 are illustrative of old types of boiler baffling arrangements. By changing the baffling to such modern designs as shown in Figures 2, 4 and 6, at least three per cent of the annual fuel bill can be saved.

Some interesting results are shown in a series of tests on a small water tube boiler of about 100 horsepower. Before improving the boiler by means of up-to-date expansion joint baffles the temperature of the gases leaving the boiler was too high and the CO_2 was too low. After installing the baffles of modern design the temperature of the gases was reduced 50°F. and the CO_2 was increased four per cent. The net result was an increase of boiler efficiency of nearly 20 per cent.

Twenty years ago boilers were baffled as shown in Figure 1. The ordinary flame plate type of baffling was used. The shaded areas in the diagram indicate the tube surface that was not effective. The correct method of baffling the same boiler with 100 per cent of the tube surface effective is shown in Figure 2.

A study of Figure 1 shows that the first pass was larger in volume than the second pass which, so far as it went, was correct in design because the gases leaving the grates are at maximum temperature and consequently they occupy maximum volume. During the process of passing through the bank of boiler tubes, the temperature of the gas reduces and simultaneously the volume of gas reduces. Consequently the second pass should not be as large in volume as the first pass. And for the same reason the third pass should not be as large in volume as the second pass. In these respects, Figure 1 is roughly all right but it is not correct like Figure 2.

In the early days, bricks were moulded to fit into the spaces between the tubes, but of course the bricks were more or less loose and there was considerable leakage of gas. About 15 years ago plastic was first introduced for boiler baffling which permitted the sloping construction shown in Figures 2, 4, and 6. This angular or tapered baffling is now used all over the world. The shaded areas, Figure 1, show what engineers call "dead regions" and show clearly why sloping baffle walls have been universally adopted. The unshaded area shows how the gas decreases in volume as it passes through the boiler. In other words, properly designed angular baffling gives a uniform gas velocity during the entire travel of the gases through the boiler. When the gases are hottest (in the furnace) they occupy a greater volume than they do after they have been cooled by passing through the boiler. That is why greater volume is required in the first pass than in the last pass. It is obvious that as the gases progress through the boiler and become cooler there is a gradual reduction in volume. Therefore by tapering the passage as is the accepted practice today the reduction in

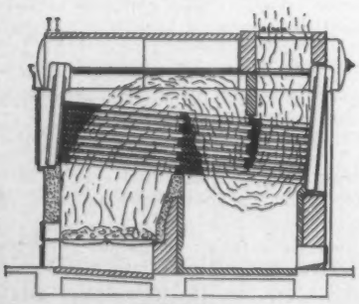


FIGURE 1

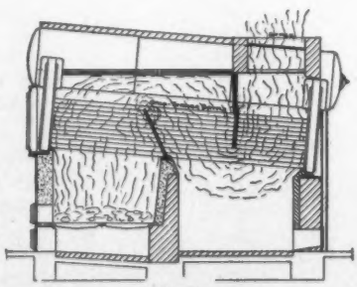


FIGURE 2

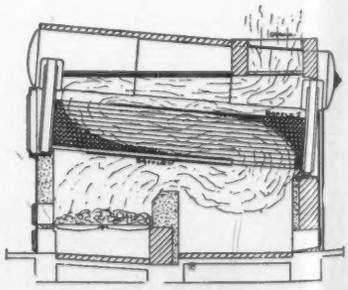


FIGURE 3

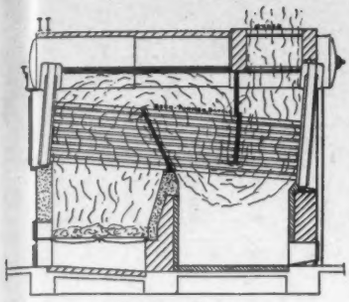


FIGURE 4

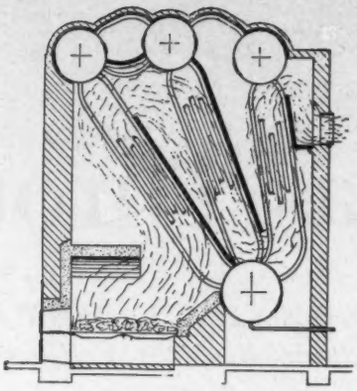


FIGURE 5

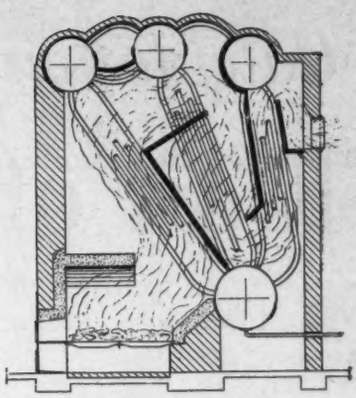


FIGURE 6

volume is cared for. Constant gas velocity is maintained throughout. Every square foot of tube surface is "active," as it should be.

HORIZONTAL WATER TUBE

Consider next the horizontal water tube boiler equipped with horizontal baffles, Figure 3. Approximately 25 per cent of the tube surface is inactive, as shown by the shaded sections. The efficiency of this type of boiler is obviously increased by the use of modern tapered cross baffles as shown in Figure 4. All leading manufacturers of horizontal water tube boilers now concede that cross baffling is superior to horizontal baffling.

Vertical boilers, also, can be improved. Figure 5 shows a Stirling type boiler equipped with old-fashioned tile baffles. Compare it with Figure 6 which shows modern cross baffle construction. The direction of the flow of gases is changed from parallel to cross flow which gives materially increased efficiency for the same reason that cross flow in horizontal water tube boilers is more efficient than parallel flow. Parallel flow has not yet been abandoned by manufacturers of all vertical type water tube boilers but it is logical that the cross flow method pictured in Figure 6 will eventually supersede the old method. Higher efficiency and less draft drop will contribute to its adoption.

Some boiler operators seem to believe that modern baffle walls are applicable only to new boilers, and that their present boilers are too old to be modernized. There is no reason why an old boiler when properly baffled and cleaned should not be as efficient as a new boiler. Even a new boiler, unless it is properly baffled and cleaned, may be less efficient than an old boiler which is clean and properly baffled. Old boilers can be made as good as new by modernizing them along the lines shown. Old metal transmits heat just as efficiently as new metal. Therefore it is logical that an old boiler, cleaned thoroughly and equipped with a better furnace and better baffling will be as efficient as when that same boiler was new.

Soot troubles can be reduced by proper baffling. Soot is evidence of incomplete combustion. A furnace of ample volume will give little soot trouble. Soot and slag generally go hand in hand. The same is true of ash. In a properly designed furnace with reduced gas velocity most of the ash is left behind in the furnace and is not carried along to settle on the tubes.

With the above in mind the question may arise. "How can be determined the length of time in which a modern baffle wall will pay for itself?" This way: Multiply the number of tons of coal burned in the furnace per year by the cost of coal per ton in dollars, multiply that by 0.03 which gives the annual saving in dollars. Divide this figure by the cost of the baffle and the result is the annual percentage on the investment.

Thus if 3000 tons of coal are burned per year, if the cost of coal is $4.00 per ton and the cost of the baffle is $800, it will be found that 45 per cent will be earned on the investment. Or, this baffle would pay for itself in a little more than ($100 \div 45 = 2.2$) two years. This rule, remember, is based on the minimum saving of three per cent. Often the modern gas tight baffle saves more than that. Three per cent is used here because it is the minimum.

The above principles are not applicable alone to water tube boilers—they are applicable to all flame boilers whether water tube, fire tube, cast iron, sheet metal, or what not. They should be given more consideration in the future than they have received in the past.

Calculation of
Flow of Gas Through Pipes

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ACCEPTED formula for loss of head due to friction due to steady fluid flow in pipes is usually given in the form $h_f = f\ (4d)\ (u^2/2g)$. This formula may be transposed into the form $p = f\ (43.5\ Lw^2/\rho D^5)$ or $p = f\ (0.00000336 Lw^2/\rho D^5)$

Older formulae used f as a constant quantity. Thus Geipel and Kilgour use a value corresponding to 0.033 for steam; Gutermuth 0.0296 for steam and 0.0104 for compressed air; Hawksley uses 0.0281; Martin, 0.0261; Hurst, 0.0260; Eberle, 0.0198; Hausbrand in "Verdampfen, Kondensieren and Kuhlen gives 0.054 for hydrogen. It was soon recognized that an invariable friction factor could not be used except over a limited range. About 1880 and shortly thereafter Gustave Schmidt in Germany, Unwin in England and later Babcock and Carpenter in America proposed formulae for f_1 varying with the diameter only. These formulae had the general form $f_1 = K(1 + b/D)$. Schmidt's formula for steam reduced to our units gives $K = 0.0019$ and $b = 7.9$ (D in inches); Babcock, for steam, used $K = 0.0027$, $b = 3.6$; Carpenter used $K = 0.0026$, $b = 3.6$; Unwin for air uses $K = 0.0028$, $b = 3.6$. The values for K were determined by Unwin on the basis of steam flowing at 100 feet per second velocity. The values of f thus obtained range from 0.013 for 12 inches to 0.068 for the Schmidt formula; 0.014 to 0.051 over the same range for Babcock or Carpenter formulae. Such values for the larger size pipe have been characterized as low by such authorities as the late Prof. Goodenough in Mark's Handbook.

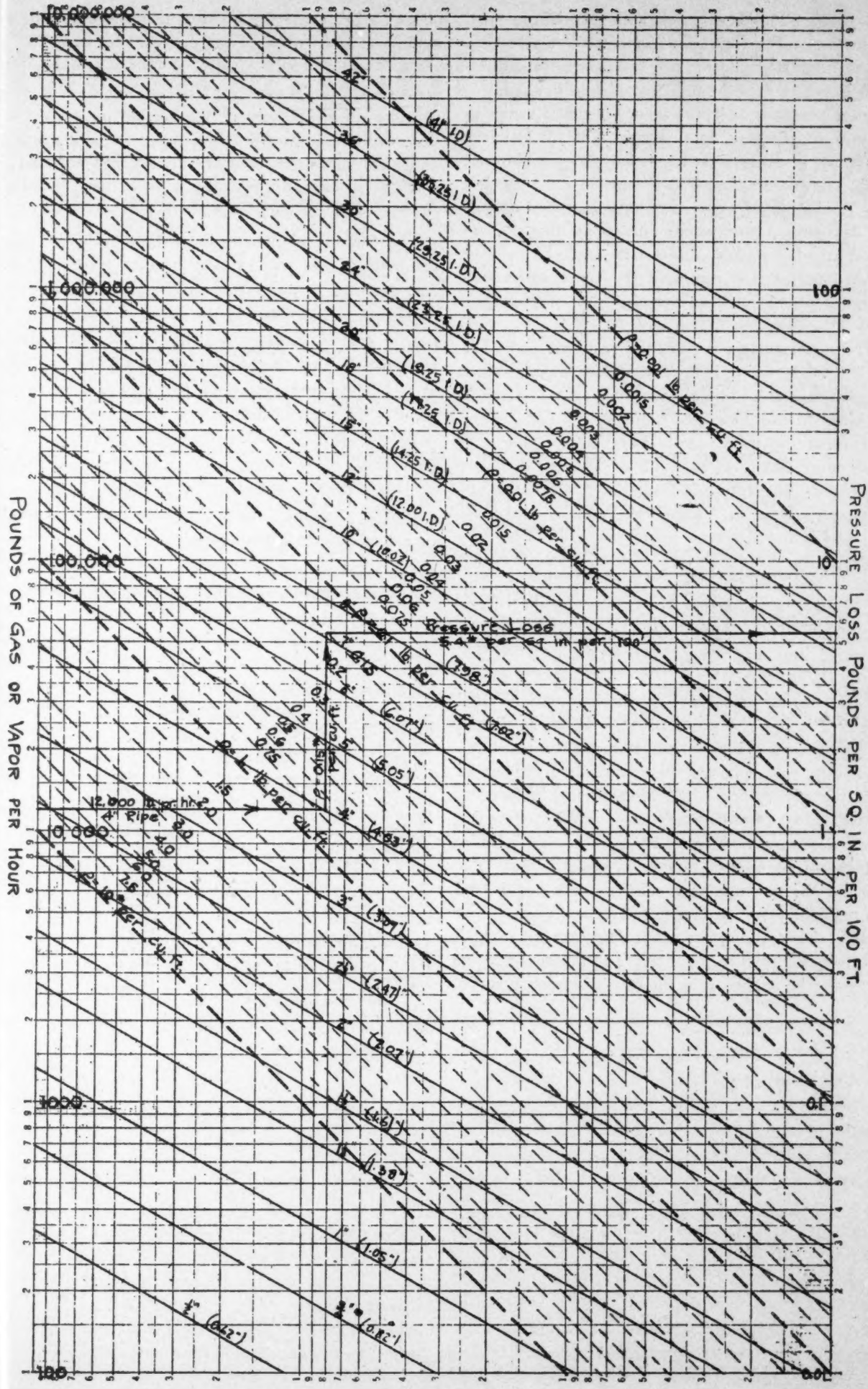
Lorenz, in Germany about 1890, derived, from a compilation of all available data for compressed air flow in pipe, a value for $f = 0.0132 d^{-0.30933}$ which results in values of f ranging from 0.028 for one-inch pipe to 0.0132 for 12-inch pipe.

From the foregoing it is obvious that the formulae which relate f to the diameter only give unsatisfactory results, and that other factors must enter. An attempt to devise such a formula was made by Fritzsche in 1908 when he devised a formula for $f = 0.0192 w^{-1/7}$. Although Fritzsche's experiments were confined to air flowing in one-inch and 1½-inch pipe 60 feet long over a wide range of temperature, pressure and velocity. The formula has been extrapolated enormously (up to

THIS discussion leads up to and presents a diagram for the solution of the problem of pressure drop for the case of steady flow of gases through pipe, covering the region of turbulent flow. The diagram is designed for the drop through 100 feet of standard size commercial pipe. The diagram is based upon the method of using a friction factor f, which is a function of the Reynold's number $(du\mu/\rho)$ applied to the general formula $h_f = f_1\ (L/d)\ (u^2/2g) = 4f_1\ (L/d)\ (u^2/2g)$. The diagram is applicable to air or steam flow problems over ordinary ranges as well as that of many other gases without correction factor. A few gases require a percentage correction, given in a supplementary table. These variations are due to variations of viscosity which in the case of gases varies as about the 0.178 power (roughly 1/6 power) of a quantity of small magnitude and consequently do not have a very great influence.

NOTATION

a = Area of cross-section of pipe in square feet.
b = Experimentally derived value used in certain friction factors.
d = Actual inside diameter of pipe in feet = D/12.
D = Actual inside diameter of pipe in inches = 12d.
f = $4f_1$ = friction factor—no units.
g = Gravitation constant = 32.2 ft. per sec.²
h_f = Frictional loss of head in feet.
K = Experimentally derived value used in certain friction factors.
L = Length of pipe in feet.
p = Pressure drop in pounds per square inch.
Q = Cubic feet of gas per second passing through pipe = w/p.
r = Hydraulic radius in feet = area/wetted perimeter = d/4 in case of circular conduits.
u = Mean velocity in feet per second.
w = Pounds of gas per second.
W = Pounds of gas per hour.
ρ = Density of gas in pounds per cubic foot.
μ = Absolute viscosity of gas in English units (poises x 0.0672).
$v = \mu/\rho$ = Kinematic viscosity in English units.
$\frac{du\rho}{\mu} = \frac{du}{v}$ = Reynolds number.


Pressure Loss, Pounds per Sq. In. per 100 Ft.
Pounds of Gas or Vapor per Hour
10,000,000
1,000,000
100,000
10,000
1000
100
100
10
1
0.1
0.01
42" (41.10)
36" (35.25 I.D.)
30" (29.25 I.D.)
24" (23.25 I.D.)
20" (19.25 I.D.)
18" (17.25 I.D.)
15" (14.25 I.D.)
12" (12.00 I.D.)
10" (11.02")
8" (7.98")
6" (6.07")
5" (5.05")
4" (4.09")
3" (3.07")
2½" (2.47")
2" (2.07")
1½" (1.61")
1¼" (1.38")
1" (1.05")
¾" (0.82")
½" (0.62")
0.0005
0.001
0.002
0.003
0.004
0.005
0.006
0.0075
0.01
0.02
0.03
0.04
0.05
0.06
0.075
0.1
0.2
0.3
0.4
0.5
0.6
0.75
1.0
1.5
2.0
2.5
3.0
4.0
5.0
Pressure Loss 1000 ft. per 64" per 100 ft.
12,000 lb. per hr. 3.0 lb. per cu. ft. 4" Pipe

$D = 48''$) with all kinds of gases, with surprisingly good results in most cases, thus showing that the factors considered in this determination of f more nearly approximated true values than anything heretofore devised.

The now generally accepted theory is that f varies as a function of $du\rho/\mu$ a fact pointed out by Osborne Reynolds, the English physicist, as early as 1883 but not generally known to or used by engineers until the last decade. A number of authorities have compiled experimental data over a wide range and by plotting the various values of f against $du\rho/\mu$ have derived average curves or equations to represent the curve so plotted. An example of an equation derived from such data is given by M. Aisenstein (Hyd. Div. A.S.M.E. Dec. 1928 Hyd. 51-7). Aisenstein derives the relation: $f = 0.167 (du\rho/\mu)^{0.170}$. The writer believes that Aisenstein's values are somewhat low especially for small values of $du\rho/\mu$ and prefers to use $f = 0.217/(du\rho/\mu)^{0.178}$ deduced by himself from the same data. This latter value corresponds more nearly to the data of McAdams of the Massachusetts Institute of Technology and also approximates the data of Hazen and Williams hydraulic tables $c = 120$ for pipe four to six years old. The general formula for flow with this value of f inserted then becomes $h_f = [0.217/(du\rho/\mu)^{0.178}]\ (L/d)\ (u^2/2g)$ and for $L = 100'$, $g = 32.2$ and D in inches, $h_f = (6.293v^{0.178}u^{1.822})/D^{1.178}(W^{1.822}/D^{4.822}.)$ This may be transformed into $p = 581\ (\mu^{0.178}/\rho)$ or $p = 0.0001926\ (\mu^{0.178}/\rho)\ (W^{1.822}/D^{4.822})$.

The last two equations are the basic equations used for the diagram. The value of $\mu^{0.178}$ being small and varying only over a limited range was taken as a constant quantity corresponding to $\mu = 12.1 \times 10^{-6}$ poundal seconds per square foot (180 micropoises) a quantity which will cover most ordinary cases within reasonable limits of accuracy, and for such cases as may require it, a table of correction factors is given. This table shows that the corrections are in the case of air and steam negligible for ordinary ranges of work. The corrections for a number of other gases are often small enough to be ignored in practice. The greatest positive correction to be applied is in the case of mercury vapor, about 25 per cent; the greatest negative for hydrogen, ammonia; and hydrocarbons, 10 to 20 per cent.

The results of the diagram should not be applied to pressure drops in excess of about 20 per cent of the absolute mean pressure of the section under investigation. Where greater pressure drops occur the pipe line under consideration should be divided into sections with smaller pressure drops using a new mean density of gas for each section.

The example shown on the diagram—12,000 pounds per hour of gas with density of 0.15 pound per cubic foot passing through four-inch pipe loses 5.4 pound pressure per 100 feet. If gas is air or steam no correction is necessary. If it had been natural gas the correction indicated in the table for methane and ethane are —7 per cent and —14 per cent, respectively, or about —10 per cent mean. As these are the most important constituents of natural gas a correction of —10 per cent is made, giving a pressure drop of 5.4 pounds —10 per cent or 4.9 pounds. If it had been mercury at 700°F. the table indicates a correction of 25 per cent or $5.4 \times 1.25 = 6.0$ pounds drop.

CORRECTION PERCENTAGES FOR p ON ACCOUNT OF VISCOSITY

Gas	Temp. °F.	% Correction	Gas	Temp. °F.	% Correction
Air	60	0	Carbon dioxide	—7	—6
Air	600	+9	Carbon dioxide	32	—5
Steam	100	—10	Carbon dioxide	210	0
Steam	500	0	Carbon dioxide	575	+7
Steam	1000	+8	Methane	32	—10
Oxygen	32	0	Methane	70	—7
Oxygen	130	+2	Ethylene	32	—12
Nitrogen	—8	—2	Ethylene	60	—11
Nitrogen	90	0	Ethylene	210	—6
Hydrogen	—8	—15	Ethyl Alcohol	212	—8
Hydrogen	212	—10	Ethyl Alcohol	413	—5
Chlorine	32	—6	Ether	32	—19
Chlorine	70	—4	Ether	97	—16
Mercury	523	+20	Chloroform	62	—11
Mercury	716	+26	Chloroform	142	0
Nitrous oxide	—6	—1	Benzine	66	—16
Nitrous oxide	212	0	Benzine	212	—8
Nitric oxide	32	—1	Ammonia	—110	—19
			Ammonia	32	—13
Nitric oxide	70	0	Ammonia	212	—6
Sulphur dioxide	32	—7	Acetylene	32	—13
Sulphur dioxide	60	—5	Ethane	—110	—19
			Ethane	32	—14
Hydrogen sulphide	32	—8	n Butane	60	—15
Hydrogen sulphide	70	—2	n Butane	212	—10
Carbon monoxide	32	—2	iso Butane	70	—16
Carbon monoxide	70	0	iso Pentane	413	—8
			iso Pentane	212	—14

The Restricted Oxidation *of* Hydrocarbon Material

I. N. BEALL
Chemical Engineer

IN this, the third of a series of articles by I. N. Beall dealing with oxidation, oil-gas conversion and other processes of synthesis, the author studies the chemistry of oxidation as it pertains to the production of the alcohols, the aldehydes, ethers, keytones, acid and acid anhydrides, dealing mostly with the possibilities as based on theory. Other theories relating to hydrocarbon oxidation and the effect of pressure and catalysts will be discussed in later articles.

CHLORINATION of hydrocarbons has received more attention than their oxidation. This is somewhat surprising as there is a similarity between the action of chlorine and that of oxygen. In fact chlorine is frequently referred to as an oxidizing agent. Chloride, however, has only one valence while oxygen has two. One chlorine atom, therefore, can only remove one hydrogen atom from a hydrocarbon to form HCl (hydrochloric acid) whereas oxygen must remove two to form H_2O (water).

Thus chlorine and methane will react to produce CH_3Cl (methyl chloride), CH_2Cl_2 (methylene chloride), $CHCl_3$ (chloroform) and CCl_4 (carbon tetrachloride) whereas oxygen under conditions where water is split off would produce H.CHO (formaldehyde), CO (carbon monoxide) and CO_2 (carbon dioxide). The double bonding power of oxygen, however, enables it to unite with both carbon and hydrogen in the same compound. In this respect, chlorine offers no parallel. The alcohols, therefore, correspond to none of the chlorinated hydrocarbons, as the distinctive grouping is

$$R_n{=}C\text{-}O\text{-}H \text{ or } R_n.C\ (OH)_n.$$

In the aldehyde formation, $R\text{-}\overset{\overset{O}{\|}}{C}\text{-}H$ the characteristic group is $\text{-}\overset{\overset{O}{\|}}{C}\text{-}H$ where the oxygen is doubly bonded to the carbon. In the other formation two carbon atoms are bonded together with one of oxygen thus, $H_3C—O—CH_3$ (methyl ether). The peroxide formation is of perculiar interest in that the oxygen is bonded to itself. The best illustration of a peroxide is hydrogen peroxide H — O — O — H which has a similarity of chemical properties corresponding to the organic peroxide

$$H_2C\overset{\overset{O}{\|}}{—}CH_2$$
$$O\underset{\underset{O}{\|}}{—}$$

(ethylene peroxide). The peroxides are unstable and because of this characteristic make excellent oxidizing agents.

Broadly classified oxygen may unite as follows with carbon and hydrogen as hydrocarbons.

1. One valence to carbon and one to hydrogen.
2. Two valences to one carbon
3. One valence to each of two carbons
4. One valence to carbon and one to another oxygen
5. One valence to carbon and one to another element

Under each broad classification there are numerous sub-classifications ending with the specific compound. Each group and sub-group has its characteristics but fortunately a great many generalities apply to the broader classifications.

THE ALCOHOLS

The alcohols are subclassified as monohydroxylic and polyhydroxilic depending upon the number of hydroxyl groups, and further as primary, secondary and tertiary, depending upon the number of alkyl or aryl radicles. In the oxidation of the saturated hydrocarbons under pressure and in the presence of a catalyst it is not likely that the oxygen combines directly to form the alcohols. In order to form the hydroxyl group, the molecule of oxygen must dissociate into atoms. If the peroxide were first formed, these peroxides which are unstable and are of themselves excellent oxidizing agents could oxidize the saturated hydrocarbons to the alcohols. The catalyst

could also effect a loose combination with molecular oxygen, and, from this loose combination, atomic oxygen could separate and combine to form the alcohols from the saturate hydrocarbons. Thus the effect of ethylene peroxide on ethylene might be considered to take place as follows:

$$C_2H_4O_2 + C_2H_6 \rightarrow C_2H_4O + C_2H_5OH.$$

The more likely result of the action of the organic peroxide would be expressed:

$$C_2H_4O_2 \rightarrow C_2H_2 + (HO)_2$$

The hydrogen peroxide thus formed reacting immediately with the ethane to produce water and an alcohol,

$$C_2H_6 + H_2O_2 \rightarrow C_2H_5OH + H_2O.$$

Under the above conditions, the acetylene would likely immediately polymerize so that there would result the water soluble layer containing the alcohol and the oil soluble layer consisting of the polymerized products of acetylene. The alcohols on dehydration yield the corresponding unsaturates as, for example, ethyl alcohol,

$$C_2H_5OH \rightarrow C_2H_4 + H_2O,$$

which on dehydration yields water and ethylene. Similarly the peroxides which are much more unstable than the alcohols would yield the corresponding hydrocarbon of the acetylene series. In either case, regardless of the starting materials, the products caused by the action of heat and pressure would be relatively complex and would separate as oil soluble and water soluble layers together with fixed gases.

The tendency of every system of chemically reactive materials on increase of temperature is to form products which are highly resistant to decomposition by heat. Water and the lower members of the hydrocarbon series are very stable towards dissociation by heat and this accounts for their occurrence in the final products from the high temperature decomposition of carbon, hydrogen and oxygen containing compounds. The oxides of carbon CO and CO_2 are also very heat stable so they are likewise to be anticipated in the end products from high temperature treatment.

The distinguishing group for the alcohols is C — O — H, that is, one of the two oxygen bonds is attached to carbon and the other is attached to hydrogen. The mean value for the terminal effect of the COH group is given by Thomsen as 4,467 calories on a gram-mol basis or on a pound-mol basis 8,041 B.t.u. The heat of formation of methane, CH_4, is given as 10,719 B.t.u. per pound mol while that of the corresponding alcohol CH_3OH (methyl alcohol) is given as 16,013 B.t.u. The difference between the two is therefore 16,013 — 10,719 = 5,294 B.t.u. The molecular weight of methane is approximately 16 and that of CH_3OH is approximately 32. On a pound basis 5294 ÷ 16 = 331 B.t.u. are given out when 1 lb. of methane burns to 2 lbs. of methyl alcohol. (Note: All calculations are made on the basis of 68°F. and in the vapor state). Roughly, considering that this reaction did go to completion and that the specific heat of the mixture was 0.5, the temperature would rise 331°F. above that at which ignition took place, if no heat were abstracted and only the stoichiometric proportions necessary to the reaction were present.

If the monohydric alcohol corresponding to saturated hydrocarbon is taken, it is found that the difference in the thermal effect is practically a constant and the same as for methane and methyl alcohol. As, for example, the heat of formation of ethane (C_2H_6) is 18,749 B.t.u. per mol while that of the corresponding alcohol (C_2H_5OH) is 24,080 B.t.u., a difference of 5,331 B.t.u. which corresponds rather closely to the difference of 5,294 B.t.u. between methane and methyl alcohol. Likewise between propane and propyl alcohol there is a difference of 5,432 B.t.u. Here again the agreement between the differences is close.

The molecular weight of the hydrocarbons increase with the ascension of the series, so there are more pounds per pound mol. The amount of heat necessary to raise the temperature a given difference also increases but the difference between the heats of formation remains practically a constant. Therefore one would not anticipate as great temperature rise on the partial combustion of propane to propyl alcohol. The temperature of reaction should be easier to control. In most of the work done on the partial oxidation of the saturated hydrocarbons very little attention has been given to the control of the temperature of reaction, nor have means been provided for the rapid dissipation of the heat of exothermic reaction. As the degree of oxidation is increased, the amount of heat evolved becomes greater. In other words more heat is evolved in the oxidation of methane to formaldehyde than in the partial oxidation of methane to methanol. In the partial oxidation of formaldehyde to formic acid, heat is again evolved and likewise in the oxidation of the formic acid to the oxides of carbon and water more heat is evolved.

THE ALDEHYDES

The aldehydes are considered to be derivatives of the alcohols similarly as the alcohols are considered to be derivatives of the hydrocarbons. The characteristics of the aldehydes is the grouping

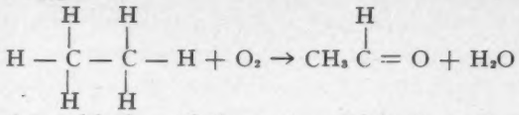
$$-\overset{H}{\underset{|}{C}}=O.$$

They are obtained from the alcohols by oxidation as follows:

$$CH_3-\overset{H}{\underset{H}{\overset{|}{\underset{|}{C}}}}-O-H + O \rightarrow CH_3\overset{H}{\overset{|}{C}}=O + H_2O$$

They may be considered as being obtained from

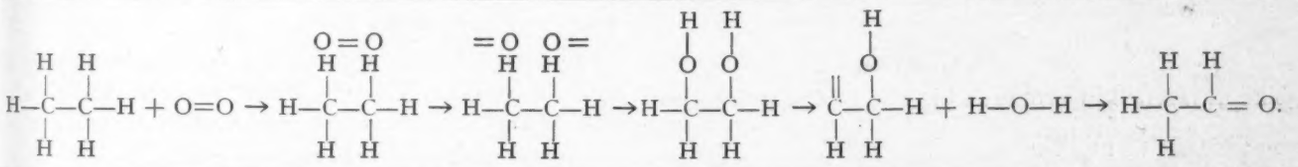
the saturated hydrocarbons by the action of molecular oxygen



In the oxidation of the saturated hydrocarbons by air or free oxygen it would seem that the only logical assumption would be an aldehyde as a primary reaction product, a theory which seems to check with results of numerous investigations. Grant that the concept of all matter as consisting of atoms and molecules is correct and that oxygen in the free state occurs in the molecular form graphically represented by the symbol, O = O, signifying that the two atoms are bound by a double bond which is electrical in nature. Before reaction could take place, the bonds between the two atoms must break. Taking the preceding equation of the reaction between ethane and oxygen for the production of acetaldehyde and water, for illustration, the following reasoning would logically apply.

1. The oxygen molecule must be brought into close physical contact with the molecule of ethane so that the chemical forces will act.

2. Granting that the six hydrogen atoms are external and the carbon atoms form the nucleus, the oxygen molecule would first contact the hydrogen atoms. Graphically this could be represented as follows:



The glow effect noted by a number of investigators when hydrocarbons are oxidized in glass or quartz tubes is probably due to some molecular rearrangement similar to those given as illustration. Such glow phenomena are common to unstable organic molecules undergoing atomic rearrangement. Molecular energy does not always have to be liberated in the form of heat waves. The evolution of light has something to do with the change in the form of energy from a higher to a lower level.

In all the oxidation reactions of the hydrocarbons which take place in the gas phase, the element of chance would play an important role. Thus one molecule of ethane might be contacted with two molecules of oxygen even tho the stoichonetric proportions were correct. In such an event, water and carbon monoxide might result

$$C_2H_6 + 2O_2 \rightarrow 3H_2O + 2\,CO$$

In order to lessen the element of chance, thorough admixing of the reactant gases should be attained in so far as possible.

Then again there is the chance that the oxygen molecule instead of attacking the hydrocarbon molecule may attack an already partially oxidized molecule. In their nascent conditions such partially oxidized molecules would probably be easily susceptible to attack by oxygen. Therefore the time element must also be given consideration as well as that of admixture. The fact that the oxidation of hydrocarbon takes place in stages may be considered as fairly definitely established, but the mechanism by which these reactions occur, is not understood. Adequate means for the control of temperature, time, catalyst and pressure must be provided, otherwise the products will be those of chance rather than of choice.

In the restricted oxidation of the hydrocarbons the chance of two or more molecules of oxygen reacting with one hydrocarbon may be lessened by using an excess of hydrocarbon. Where resorted to, such procedure has been found to give improved yields of oxygen-containing hydrocarbons. There is also the added assurance against overheating because of the mass of non-reacting hydrocarbon absorbing the heat of reaction. The chance of pyrolysis is therefore diminished.

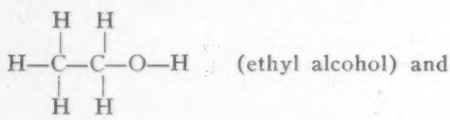
In chemical reactions that take place in the liquid phase, the difficulties of heat dissipation are not as great as for those that take place in the gaseous state, inasmuch as cooling may be accomplished by cooling coils and agitation. Then again the efficiencies of heating or cooling surfaces are many times higher for a liquid than a gas. However, in all such reactions that take place in the liquid phase, where the reactions are exothermic, temperature control must be provided, otherwise the reaction goes "wild." The same is true of reactions that take place between gases, and it is not readily apparent why the majority of investigators have neglected this point in studying the oxidation mechanisms of the paraffin hydrocarbons. If means for heat dissipation are not provided, it is difficult to foresee how the products of any extensive hydrocarbon oxidation could be other than those of pyrolysis. It is one thing to initiate a reaction but it is another to control it once initiated.

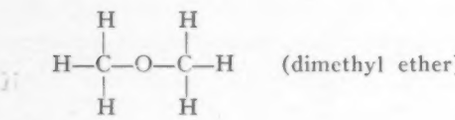
In the formation of the aldehydes from the corresponding saturated hydrocarbons, a large amount of heat is evolved. This heat must be dissipated rapidly otherwise the temperature of the mixture will rise to the point where "cracking" will occur. If "cracking" is the objective, well and good; the less

cooling the better; but, if aldehydes are the objective, cooling should be provided. The average difference between the heat of formation of the corresponding alcohols and aldehydes is approximately 1,692 B.t.u. per lb. mol; between the corresponding aldehyde and saturated hydrocarbon 9,733 B.t.u. The thermal effect associated with the group H—C=O is an average of 11,678 B.t.u. It is obvious that the control of temperature cannot be overemphasized in so far as it pertains to the oxidation of hydrocarbons to oxygen-containing hydrocarbon derivatives.

ETHERS, KETONES, ACIDS AND ACID ANHYDRIDES

The oxidation of the saturated hydrocarbons may yield higher oxidation products as well as the alcohols and aldehydes. The empirical formulae of the ethers correspond to the alcohols, the difference in properties are due to the architectural arrangement of the atoms. Thus the empirical formula for dimethyl ether and ethyl alcohol may both be expressed as C_2H_6O but graphically they are written


(ethyl alcohol) and

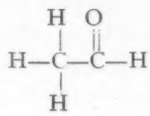

(dimethyl ether).

The difference in properties is due to the two carbon atoms being attached to the oxygen in the ether whereas in the alcohol the oxygen is attached to a hydrogen and a carbon. Organic chemists regard the ethers as derivatives of the alcohols in which the hydrogen atom has been replaced by the alkyl radicle. Thus, for illustration, CH_3—O—H (methyl alcohol) or CH_3—O—CH_3 (dimethyl ether) in which the group CH_3 replaces H. The ethers are normally obtained from the dehydration of two molecules of alcohol, thus:

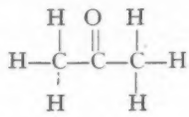
$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O$$

In any oxidation of the saturated hydrocarbons by means of oxidizing agents other than free oxygen, the alcohol formation would likely take precedence over that of the ethers. However, if such oxidations took place in the presence of dehydrating agents such as alumina, sulfuric acid, phosphoric acid, phosphorus pentoxide, etc., ethers would likely appear in the reaction products. The possibilities suggest a fertile field for research. Ether was once used to a considerable extent to give "pep" to gasoline. Some of the higher ethers than the diethyl ether used might prove valuable as an ingredient of motor fuel. There are also possibilities in the use of higher alcohols in a similar manner.

The aldehydes are the first product of oxidation of the primary alcohols. The ketones are the primary oxidation product of the secondary alcohols. There is a marked resemblance in characteristics between the aldehydes and ketones because of the double bonding of the oxygen to the carbon atom. The differences are due to the replacement of the hydrogen by an alkyl or aryl radicle. Thus the symbolic formula for acetaldehyde is:



whereas that of acetone is:



Both aldehydes and ketones resemble the unsaturated hydrocarbons in their ability to form additive compounds. Both are active chemical and decompose easily by heating under pressure. On decomposition by heat under pressure, oil soluble liquids and water soluble liquids separate. Reid and Herndon decomposed acetaldehyde at 325°C and acteone at 400°C and obtained oil soluble and water soluble layers and also fixed gases.

The formulae for the ketones require three or more carbon atoms. That is, there must be a carbon to which the oxygen is attached and at least two radicles containing a carbon atom each.

The lowest hydrocarbon, therefore, that could be used for the production of a ketone by direct oxidation would be propane. Thus acetone might be considered as a direct oxidation product of propane in accordance with the reaction:

$$CH_3 \cdot CH_2 \cdot CH_3 + O_2 \rightarrow CH_3 \cdot CO \cdot CH_3 + H_2O$$

with butane,—

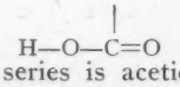
$$C_2H_5CH_2 \cdot CH_3 + O_2 \rightarrow C_2H_5CO\ CH_3 + H_2O$$

and with pentane,

$$C_2H_5 \cdot CH_2 \cdot C_2H_5 + O_2 \rightarrow C_2H_5COC_2H_5$$

It is probable that the undirected reactions of oxygen with members of the paraffin series higher than ethane would produce both the ketones and the aldehydes.

The carboxylic acids represent a higher stage of oxidation than the aldehydes and ketones. The simplest monocarboxylic acid is formic acid having the formula H.COOH. The characteristic grouping for the series is:



The next in the series is acetic having the for-

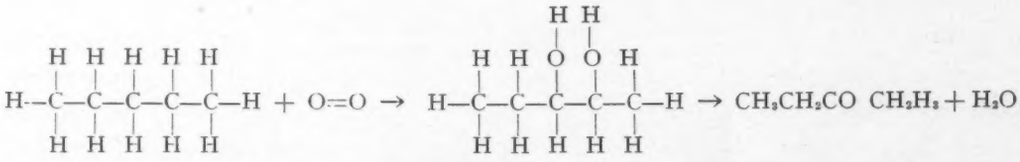
mulae CH_3COOH. The acid anhydrites may be considered as derivatives of two molecules of the acid from which water has been abstracted.

$$\begin{matrix} CH_3\ COO \\ CH_3\ \ CO \end{matrix}\Big\rangle H\ OH \rightarrow \begin{matrix} CH_3\ C = O \\ \quad\ \ O \\ CH_3\ C = O \end{matrix} + H_2O$$

The grouping $\begin{matrix} -C = O \\ \quad\ \ O \\ -C = O \end{matrix}$ is characteristic of this series of compounds. They represent a still higher stage of oxidation than that represented by the carboxylic acids.

The end products representing the highest stage of hydrocarbon oxidation are carbon dioxide and water. These are the products of unrestricted combustion such as occurs in an open flame.

The hydroxylation theory has been widely accepted as accounting for the mechanism of the oxidation reactions of the paraffin hydrocarbons. It has also been widely criticised because the hydroxy derivatives have not been identified in the products of restricted oxidation. In support of the hydroxylation theory, it might be stated that the non-appearance of the primary alcohol cannot be taken as evidence that the hydroxyl formation does not occur. In any oxidation wherein free oxygen is used, it is in the molecular form. It is logical to assume that the two atoms of oxygen in one molecule would attack the hydrocarbon at one point. Therefore, two hydroxyl groupings would exist at one point in the hydrocarbon at the moment of primary reaction and thus produce an unstable formation. Oxygen is bound to itself until the bonds break. At the moment of rupture reaction would occur. Take, for example, in a long chain hydrocarbon such as, for illustration, normal pentane:



The two hydroxyl groups occurring in proximity to each other would cause water to split off and there would be formed an aldehyde or ketone. The recognition of the aldehyde or ketone in the end product would not disprove that hydroxylation had not taken place.

In reactions where an atom of oxygen is transferred, one might expect to find methyl alcohol as a product of the oxidation of methane, ethyl alcohol from the oxidation of ethane, etc., but not in the action of free oxygen in the molecular form.

Other theories relative to hydrocarbon oxidation and the effect of pressure and catalysts will be discussed in subsequent articles dealing with the subject.

Simple Safety Device Stops Uncooled Engine

At the combination plant operated by Charles E. Knox near Covington, Oklahoma, where a small crude skimming unit is operated in conjunction with a natural gasoline plant, a simple safety device has been developed to stop the compression equipment whenever the water supply is cut off. This "sure shot trouble stopper" effectively removes danger of damaging the machine, by a simple method of cutting out the magneto.

Water in circulation through the engine jackets of the compression and power cylinders is maintained under pressure. Normally this pressure is about 15 pounds and to prevent overheating in the event the pump should loose suction, a magneto cut-out is provided to shut the engine down. A 30-pound pressure gauge is placed on a connection just under the power cylinder. The glass was removed from the gauge and a small hole was drilled at a point near the zero indication on the dial. A cable leads from the short-out connection on the magneto to the pressure gauge, where it is fastened with a small screw so that the end of the cable when in position forms a stop for the indicator hand of the pressure gauge. As long as the water pressure is above zero pounds the engine continues to operate, but if for any reason the water pressure drops to zero the hand on the pressure gauge drops against the improvised stop and the magneto instantly ceases to function, thus stopping the engine and preventing damage to the compression machinery.

Flash Tower

Removes Water and Sand

PROCESSING Wilbarger County and South Electra crude containing on an average of two per cent of salt water and sand has in the past caused Dale Oil & Refining Company many days of shut down time in cleaning out the first shell still and the lines leading to it. After several experiments, an installation was placed in the refinery which has since proven very beneficial in removing from two to five tons of salt and sand each week before the oil in process reaches the shell battery of stills.

In the flow sheet layout, the oil was previously pumped through a large heat exchanger in counter flow with the residuum from the evaporator which stripped the oil from the pipe still after the light cuts were removed in the shells. Low pressure was maintained on the charging stock, which, when permitted to acquire sufficient heat to vaporize the water, carried the salt in suspension together with the entrained sand directly to the first shell still where it was deposited. In consequence, it was necessary to shut down this unit on an average of every 10 days to clean out the accumulation in the shell. This not only delayed the operation of the plant, but was quite detrimental to the life of the still bottom, causing it to blister, and the deposit of the sand and salt accelerated the formation of coke.

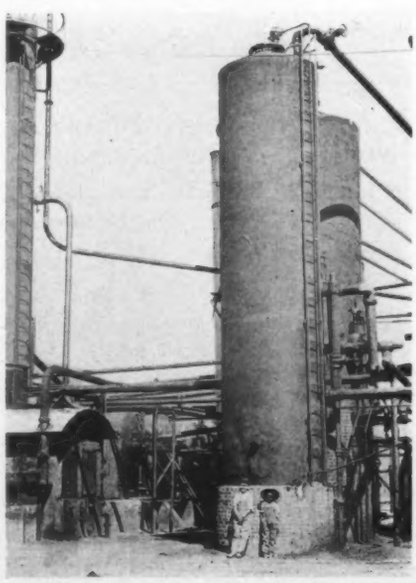
In the vapor line between the vaporizer and the bubble tower, a Southwestern type Y210 exchanger was placed on a tower so that the line of flow of the charging stock could be pumped through the tubes. Picking up a temperature through the old heat exchanger and this new one of 240° F. the oil was led through an economizer, built so that the hot gases from the furnaces of the shell stills could be utilized to heat the oil to a still higher temperature.

A primary flash tower was placed in the line between this economizer and the first shell still to receive the oil at an average temperature of 290° F. Up to this tower, the oil is carried at 45 pounds pressure, maintaining practically all the water as a liquid carrying the salt in solution. Using a gate valve to reduce the pressure, it is opened just enough to maintain the required back pressure on the oil until it reaches it, then, after passing through the gate, the charging stock has the pressure released sufficiently to permit the water to flash into steam.

This flash tower performs a double service: it removes a part of the light vapors in the oil; and serves as a drum which receives the sand and salt which have been released into it. Since its installation, practically all the sand and salt has been accumulated in it, rather in the first shell still under the previous method of operation. A by-pass line leading around this tower allows the operators to cut it out of service when the accumulation of sand and salt has been built high in the base of it. A blow-off line leads from the lower head of the tower which serves to remove the principal part of the accumulation, but occasionally the sand builds up and blocks off this drain valve.

Since this device has been placed in operation the first shell still has been taken out of service periodically for inspection; but there has been no accumulation of consequence in it, either of sand, salt or coke. George Jennings, plant superintendent, says that occasionally, depending upon the condition of the charging stock, he has removed as much as 15 tons of salt and sand from primary flash tower in a week's time.

Showing, at right, the primary tower which acts as a sand and salt accumulation drum in the Dale Oil & Refining Company's plant at Electra, Texas.



Enough Refinery Capacity

...But It Is Not All Modern

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WITH the exception of the year 1926, the petroleum refining industry has shown an increase in rated capacity in each of the 12 annual reports of the Bureau of Mines. During the past five years, however, this growth in capacity has been increasingly small until the difference in capacity in 1932 as compared to 1931 is but 32,743 barrels. This was sufficient to bring the total rated capacity to 4,020,428 barrels per day. Apparently economic conditions are finally and actually discouraging expansion of crude running facilities; which expansion could well have been stopped in 1929 when the industry was operating at 78 per cent of its capacity, as against 65 per cent in 1931.

TABLE I

	Crude Runs to Stills* 1932 Barrels	1931 Barrels
January	68,715,000	70,207,000
February	63,814,000	65,314,000
March	68,502,000	73,651,000
April	71,131,000	74,761,000
May	74,669,000	78,521,000
Five Months	346,831,000	362,454,000

*Bureau of Mines monthly petroleum reports.

Since 1929 the number of refineries has grown from 427 to 479. Operating plants have increased from 341 to 365, but on the other hand, the shut-down refineries have mounted in number from 72 in 1929 (54 in 1930) to 108 at the beginning of 1932.

During the same four-year period, operating capacity has been steadily increasing, despite gathering economic storm clouds, (and subsequent deluge). With operating capacity in 1929 of 3,325,890 barrels, increases were shown in 1930, again in 1931, when operating capacity was 3,706,610 barrels, but dropped back to the 1930 level of 3,622,092 barrels at the beginning of this year. Capacity shut-down has increased from 130,760 barrels in 1930 to 389,616 barrels in 1932. However, construction figures (speaking only of new crude oil processing units) have been decreasing. With 99,000 barrels of new capacity building (14 plants) at the beginning of 1929, only 8720 barrels (six plants) was reported at the beginning of 1932. Perhaps this is to be taken as some indication of recognition by the industry that further expansion of crude treating facilities is not warranted.

According to the annual survey of refineries in the United States as of January 1, 1932, now ready for distribution by the Bureau of Mines (I. C. 6641), in 1931, the average total capacity of the operating plants amounted to 3,744,000 barrels, and the daily average crude throughput was 2,450,000 barrels. This indicates that the refineries operated at an average of 65 per cent of capacity, compared with 69 per cent in 1930, and 78 per cent in 1929. This continued decreasing in percentage of operated capacity, the continued increase in shut-down capacity, and increase in the number of shut-down refineries (even though many of them are so obsolete as to be impractical in operation) can well be interpreted as a "stop signal" in so far as further expansion of the crude oil processing ability of the industry is concerned.

The foregoing does not mean that the refining industry will be able to "rest on its laurels" for a period of years, engaging in no major construction programs. Present operating capacity of the industry is between 30 and 40 per cent obsolete, worn out, or hazardous of operation. Competitive conditions within the industry will bring about the continued installation of additional modern distillation facilities. In order to compete with other units the going concern must take advantage of developments in distillation, both vacuum and atmospheric, in fractionation where scientific research bids fair to cause some additional changes through improvements and in stabilization and rectification.

Present conditions in this industry, and the trend in motor fuel manufacture and motor fuel demand, do however, point to continued difficulty in profit making for the refinery not equipped with skimming, cracking, and stabilization facilities. Despite the fact that these conditions and these trends which have caused widespread activity in construction of cracking and naphtha reforming (cracking) units, and stabilization systems for the past two years, the number of skimming plants increased from 242 in 1930 to 259 in 1931 and again increased from 259 in 1931 to 299 in 1932 (as of January 1)—an increase of 40. Something of the hazard involved in this phase of the industry is shown in the analysis of the status of these plants. On January 1, 1931, 190 skimming plants where operating, 60 were shut down, nine where building, whereas at the beginning of this year, 208 skimming plants were operating, 86 were shut down and only five were building. Of the total of 299 plants classed as skimming, 86 were shut

down. Breaking-down further it is found that 119 skimming plants are equipped with cracking units and of this number only 21 were shut down at the beginning of this year. On the other hand, there were 180 straight skimming plants, not having cracking facilities, and of this number 65 were shut-down. Compared with previous year the number of non-cracking skimming plants now inoperative is greater than in any previous year. It is this group of refineries for which operation at a profit is becoming increasingly difficult and trends of the industry point to the fact that entry into this field is becoming increasingly hazardous.

PLACE FOR SMALL PLANTS

Without question there is a place in the refining industry for the independent or small refinery and there is a place for the skimming plant not equipped with cracking facilities, but the place of this latter group is rapidly becoming restricted and untenable because of factors not governable by the industry. The influencing factor of most importance in this connection is that of increasing production of small cars of high compression ratio, and the increasing compression ratio of larger automobiles, which demand of the refiner that he produce a motor fuel of higher octane rating than is possible through straight skimming methods.

The place or position of the independent refiner, especially those not owning or controlling marketing outlets and are dependent upon the jobber or wholesaler for the movement of motor fuel, kerosene, furnace oils, fuels and the like, can be strengthened only through the manufacture of products capable of competing with quality products secured by efficient facilities of larger and perhaps more modern plants in his territory. It is difficult to dodge the issue that skimmed gasoline of 50 to 55 octane value will not compete with 60 to 65 octane regular motor fuel sold and demanded to satisfactorily perform in the modern motor car. There are 155 companies manufacturing petroleum products but not employing the cracking unit and in the face of present demands of the marketing branch of the industry, and current commercial specifications calling for definite octane ratings, it appears that further application of the cracking process is necessary.

SCALE OF OPERATIONS

While the foregoing discussion has had to do with a comparison of the industry during the years 1930, 31 and 32, it is interesting to note that the operations by months, during this year, closely approximate the operations for the first five months of 1931. During the first five months of this year refiners have processed 15,623,000 barrels less of crude oil than during a like period of 1931. Due to increased recovery of gasoline, both by skimming and cracking, total production of gasoline during the first five months of 1932 was but 3,688,000 barrels less than the same period last year.

A study of reports available covering operations through May, reveals that the refining industry is operating, on an average, the same number of refineries and further, it is operating at about the same percentage of capacity as last year. The average number of operating plants reporting each month this year has ranged from 338 to 347, or an average of 343 plants. Compared with the first five months of last year, the average for the five months is the same, although the average monthly range of operating plants reported monthly was from a low of 335 to a high of 356.

For both periods the average number of plants operating monthly was 343, whereas the average percentage of capacity operating for the first five months of 1931 was 64.5 per cent, as compared to the same period this year when average percentage of capacity operated dropped to 63. The refining industry in 1932 has been operating from a low of 60 per cent of capacity in operation in January and February, to 67 per cent of capacity in April and May, which was the same percentage in operation during April and May of 1931.

During the five months period the industry processed 362,454,000 barrels of crude oil in 1931 as compared to 346,831,000 barrels in 1932. This represents a decrease in total crude processed of 15,623,000 barrels, or about 3,000,000 barrels less crude per month, on an average.

From the crude oil processed in the first five months of 1931, the industry produced 87,105,000 barrels of straight run gasoline (21.2 per cent recovery) and 69,758,000 barrels of cracking gasoline (19.2 per cent recovery), which totals 156,863,000 barrels (40.4 per cent recovery) for the period.

During the same period this year refineries have produced 83,685,000 barrels of straight run gasoline (24.2 per cent recovery) and 69,470,000 barrels of cracked gasoline (20.0 per cent recovery) from the 346,831,000 barrels of crude run, or a total of 153,165,000 barrels of motor fuel, which represents 44.2 per cent recovery. The difference in volume of gasoline produced for the two five-month periods is 3,698,000 barrels (less in 1932).

These comparisons indicate that the refining industry, operating about the same number of refineries as last year, and operating at about the same percentage of total capacity has, through various contributing factors, been able to secure an increased recovery of about four per cent gasoline over the same period last year, and has run over 15,000,000 barrels less of crude and produced but about 3,500,000 barrels less gasoline. Consumption of natural gasoline has shown a marked decrease so far this year.

Contributing to the increase in straight run gasoline recovery as compared to the first five months of last year, is the larger production and consumption of lighter crudes in this country and a tendency to cut deeper into the crude at refineries where naphtha reforming (cracking) units have been installed during the past year, and also the operation of several new skimming plants, in light oil fields.